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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: Registration Standard for Glyphosate

FROM: Stephen J. Simko
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S Simko

TO: Robert J. Taylor
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THRU: David J. Severn, Chief
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David Severn

Enclosed find the final Phase II documents of the Registration Standard for Glyphosate.

cc: A. Rispin (SIS)

TABLE A
GENERIC DATA REQUIREMENTS FOR GLYPHOSATE

Data Requirement	Composition 1/	Use Pattern 2/	Does EPA Have Data To Satisfy This Requirement? (Yes, No or Partially)	Bibliographic Citation	Must Additional Data Be Submitted Under FIFRA Section 3(c)(2)(B)? 3/
158.130 Environmental Fate					
DEGRADATION STUDIES-LAB:					
61-1 - Hydrolysis	TGAI or PAIRA	A,B,C,D,F,G,H	YES	00108192	NO
Photodegradation					
61-2 - In water	TGAI or PAIRA	A,B,C,D,G	NO	—	YES
61-3 - On soil	TGAI or PAIRA	A,G	NO	—	YES
61-4 - In Air	TGAI or PAIRA	A,F	NO	—	YES
METABOLISM STUDIES-LAB:					
62-1 - Aerobic Soil	TGAI or PAIRA	A,B,F,G,H	NO	—	YES
162-2 - Anaerobic Soil	TGAI or PAIRA	A	NO	—	YES 4/
162-3 - Anaerobic Aquatic	TGAI or PAIRA	C,D	NO	—	YES
162-4 - Aerobic Aquatic	TGAI or PAIRA	C,D	NO	—	YES
MOBILITY STUDIES:					
163-1 - Leaching and Adsorption/Desorption	TGAI or PAIRA	A,B,C,D,F,G,H	PARTIALLY	00108192	YES
163-2 - Volatility (Lab)	TEP	A,F	NO	—	YES
163-3 - Volatility (Field)	TEP	A,F	NO	—	YES 6/

1/ Composition: TGAI = Technical grade of the active ingredient; PAIRA = Pure active ingredient, radiolabelled; TEP = Typical end-use product.
2/ The use patterns are coded as follows: A-Terrestrial, Food Crop; B-Terrestrial, Non-Food; C-Aquatic, Food Crop; D-Aquatic, Non-Food; E-Greenhouse, Food Crop; F-Greenhouse, Non-Food; G-Forestry; H-Domestic Outdoor; I-Indoor.
3/ Data must be submitted no later than _____.
4/ Not required if an acceptable anaerobic aquatic metabolism study is conducted.
5/ Requirement is contingent upon the results of studies in 162-1 and/or studies in 164-1 and 164-2.
6/ Deferred pending receipt of acceptable laboratory volatility data.
7/ No data required because of low toxicity and exposure from present use pattern

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Data Requirement	Composition 1/	Use Pattern 2/	Does EPA Have Data To Satisfy This Requirement? (Yes, No or Partially)	Bibliographic Citation	Must Additional Data Be Submitted Under FIFRA Section 3(c)(2)(B)? 3/
§158.130 Environmental Fate (continued)					
DISSIPATION STUDIES-FIELD:					
164-1 - Soil	TEP	A,B,H	NO	—	Yes
164-2 - Aquatic (Sediment)	TEP	C,D	NO	—	YES
164-3 - Forestry	TEP	G	NO	—	YES
164-4 - Combination and Tank Mixes					
164-5 - Soil, Long-term	TEP	A,C	NO	—	YES 5/
ACCUMULATION STUDIES:					
165-1 - Rotational Crops (Confined)	PAIRA	A,C	NO	—	YES
165-2 - Rotational Crops (Field)	TEP	A,C	NO	—	YES
165-3 - Irrigated Crops	TEP	C,D	NO	—	YES
165-4 - In Fish	TRAI or PAIRA	A,B,C,D,G	NO	—	YES
165-5 - In Aquatic Non-Target Organisms	TEP	A,B,C,D,G	NO	—	YES
Subpart K Re-entry	TEP 7/				

DYNAMAC
CORPORATION

GLYPHOSATE

Final Report

Task 2: Environmental Fate and Exposure Assessment

Contract No. 68-01-6679

JUNE 7, 1985

Submitted to:
Environmental Protection Agency
Arlington, VA 22202

Submitted by:
Dynamac Corporation
Enviro Control Division
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[^{14}C]Glyphosate (94% glyphosate, 5.9% aminomethylphosphonic acid) and aminomethylphosphonic acid were stable in sterile buffered water at pH 3, 6, and 9 during 35 days of incubation in the dark at 5 and 35 C (Brightwell and Malik, 00108192). Slight degradation of [^{14}C]glyphosate was observed in two of three sterile, natural waters treated with [^{14}C]glyphosate (94% glyphosate, 5.9% aminomethylphosphonic acid), at 0.1 ppm, and incubated in the dark at 30 C for 35 or 49 days. Aminomethylphosphonic acid was detected at maximum concentrations of 25.3 and 17.2 % of the applied 35 days posttreatment in the Cattail Swamp (pH 6.2) and Ballard Pond (pH 7.3) waters, respectively. No degradation was observed in Sphagnum Bog water (pH 4.2).

Under aerobic aquatic conditions, [^{14}C]glyphosate (94% glyphosate, 5.9% aminomethylphosphonic acid) degraded in three natural waters at pH 4.2, 6.2, and 7.3, with 39-49% of the applied remaining at 49 days, 51-61% at 63 days, and 58-69% at 35 days, respectively (Brightwell and Malik, 00108192). Respective aminomethylphosphonic acid concentrations increased steadily at each sampling interval, reaching maximum concentrations in the Sphagnum Bog, Cattail Swamp, and Ballard Pond waters of 26.2, 30.2, and 23.1% of the applied radioactivity. A maximum of 29, 14.6, and 11.4% of the applied radioactivity evolved as $^{14}CO_2$ in the pH 4.2 (day 63), pH 6.2 (day 63), and pH 7.3 (day 35) waters, respectively. Addition of sediment to the system increased the dissipation of glyphosate and aminomethylphosphonic acid from water via adsorption to sediment. Evolution of $^{14}CO_2$ was not affected. All samples were maintained at 30 C in the dark.

[^{14}C]Glyphosate (94% glyphosate, 5.9% aminomethylphosphonic acid) was adsorbed to Drummer silty clay loam, Ray silt, Spinks sandy loam, Lintonia sandy loam, and Cattail Swamp sediment with Freundlich K values of 62, 90, 70, 22, and 175, respectively (Brightwell and Malik, 00108192). The maximum percentages of applied glyphosate desorbed were 5.3, 3.7, 3.6, 11.5, and 0.9%, respectively. Sphinx sandy loam soil, treated with [^{14}C]glyphosate at ~0.1 µCi/g, adsorbed 16.5 nMoles/g of [^{14}C]glyphosate (test substance uncharacterized) during 4 hours of mixing in a 15:1 water:soil slurry (Sprankle, et al., 00076493). The addition of various concentrations of phosphate to the soil had no discernible effect on glyphosate adsorption. [^{14}C]Glyphosate (purity unspecified) at concentrations ranging from 0.21 to 50.1 ppm, was highly adsorbed to five soils with organic matter contents ranging from 2.40 to 15.50% (Monsanto Co.,

00108140). Adsorption of glyphosate ranged from 71% (Soil E, 2.4% organic matter, pH 7.29) to 99% (Soil C, 15.5% organic matter, pH 5.35).

[^{14}C]Glyphosate (94% glyphosate, 5.9% aminomethylphosphonic acid) was slightly mobile to relatively immobile with <7% of the applied ^{14}C detected in the leachate from 30-cm silt, sand, clay, sandy clay loam, silty clay loam, and sandy loam soil columns eluted with 20 inches of water (Brightwell and Malik, 00108192). Aged (30 days) [^{14}C]glyphosate residues were relatively immobile in silt, clay, sandy clay loam soils with <2% of the radioactivity detected in the leachate following elution with 20 inches of water. Both glyphosate and aminomethylphosphonic acid were detected in the leachate of aged and unaged soil columns.

Neither glyphosate nor aminomethylphosphonic acid were detected (<2.5 ppb) in two canal waters flooded ~6 months following treatment of glyphosate (test substance uncharacterized), at 5 lb ai/A, to two earthen-bottom dry canals located in Washington (Kramer, 00039381-A). Soil samples taken the day before the canals were filled (~6 months posttreatment) contained ~0.35 and 0.8 ppm glyphosate and aminomethylphosphonic acid, respectively, in each canal. Glyphosate (4 lb/gal, formulation unspecified) dissipated from a pond in Florida, treated at 460 ppb, with a half-life of between 14 and 21 days (Blackburn, 00039381-E). Less than 1% of the applied was detected in the pond water 127 days posttreatment. Glyphosate was detected at a maximum concentration of 0.46 ppb in bottom sediments sampled 63 days posttreatment. The glyphosate degradate aminomethyhlphosphonic acid was not detected (<2.5 ppb) in bottom sediments.

Glyphosate and aminomethylphosphonic acid concentrations, during the 55 days after treatment with glyphosate (test substance uncharacterized) at 3.0 lb ai/A, ranged from <0.05 to 0.77 ppm (exposed soil); <0.05 to 1.28 ppm (covered soil); <0.05 to 0.55 ppm (sediment); <0.002 to 3.22 ppm (drip water); <0.002 to 0.15 ppm (stream water samples); 0.17 to 89.00 ppm (foliage); and 0.20 to 11.00 ppm (leaf litter) (Danhaus, et al., 00093922; Edwards, 00084657). N-nitrosoglyphosate was not detected in any samples, except the stream water, where 0.002 ppm were detected in all samples.

[^{14}C]Glyphosate residues in 4-week-old soybeans grown in aged (16-weeks) water-extracted and unextracted silt, sandy loam, and silty clay loam soils treated

with [^{14}C]glyphosate (purity ~96%) at 4 ppm ranged from 0.76 to 4.12 ppb (Rueppel, et al., 00108182; Henshall, et al., 00108183). Glyphosate residues in the soil during the growing period ranged from 0.64 to 3.72 ppm.

[^{14}C]Glyphosate residues (uncharacterized) accumulated in catfish exposed to N-phosphonomethyl-labeled [^{14}C]glyphosate (~98% pure) for 28 days, with a maximum bioconcentration factor of 1.87x and 13.75x in edible and visceral tissue, respectively (Monsanto Co., 00108173-A). Accumulated [^{14}C]glyphosate residues were depurated fairly rapidly with ~76% of the residues detected after 28 days of exposure being eliminated after 28 days in untreated water. [^{14}C]Glyphosate residues (uncharacterized) accumulated in the whole-body tissue of marsh clams with a maximum bioconcentration factor of ~31x in a static exposure system containing N-phosphonomethyl-labeled [^{14}C]glyphosate (>97% pure) (Monsanto Co., 00108173-E). Only 25% of the accumulated [^{14}C]glyphosate residues were eliminated after a 21-day depuration period.

Dermal, ocular, and inhalation exposures to workers may occur during application. The primary potential for exposure from the SC/L formulation is during mixing and loading where both dermal and ocular exposure can occur via splashing. Inhalation and dermal exposure may occur during application of RTU and PrL formulations. Application from aircraft increases the potential for exposure of humans and nontarget organisms to glyphosate due to spray drift and volatilization. Exposure to all formulations during application is expected to be mainly dermal. The use of protective clothing during handling, mixing, and application operations should minimize the potential for exposure to all formulations. However, data are not available to assess such exposures. Currently, no federal or state reentry intervals have been established for glyphosate.

Reported pesticide incidents involving glyphosate alone between 1966 and 1980 included 91 involving human exposure (84 people received medical attention), 2 involving domestic animals, and 1 involving environmental contamination. Most incidents occurred at agricultural and home/domestic sites. Agricultural site incidents occurred primarily during mixing/loading or ground spraying, while incidents at home/domestic sites primarily involved accidental ingestion of the pesticide. Commonly reported exposure syptoms included dermal irritation, nausea, and dizziness.

In summary, glyphosate and its degradate aminomethylphosphonic acid are stable to hydrolysis in sterile, buffered water at pH 3, 6, and 9. In three natural waters (pH 4.2, 6.2, and 7.2), glyphosate degraded with half-lives of <50, ~63, and >35 days, respectively. Addition of sediment to the three natural water systems increased the rate of dissipation of glyphosate from water via sorption to sediment. Glyphosate dissipated in pond water with a half-life of between 14 and 21 days. In two canal waters, glyphosate was not detected ~6 months posttreatment. Glyphosate and aminomethylphosphonic acid dissipation rates and concentrations in treated forests soils are extremely variable, ranging from <0.002 ppm in stream water samples to 89 ppm in foliage samples. Based on available data that indicate glyphosate is strongly adsorbed to soil, the potential of glyphosate to contaminate groundwater is expected to be low. Glyphosate has a potential to contaminate surface waters because of applications to aquatic sites. Glyphosate residues have a low potential to bioaccumulate in the edible and visceral tissue of catfish, or in the whole-body tissue of clams. Glyphosate residues do have the potential to accumulate in soybean seedlings.

The following data are required (EPA Data Requirements for Registering Pesticides) to fully assess the environmental fate and transport of, and the potential exposure to glyphosate: photodegradation studies in water, on soil, and in air; aerobic and anaerobic soil metabolism studies; aerobic and anaerobic aquatic metabolism studies; adsorption/desorption studies; laboratory and possibly field volatility studies; terrestrial, forestry, and possibly long-term field dissipation studies; accumulation studies on rotational and irrigated crops, fish, and possibly aquatic nontarget organisms; and reentry studies.

Hydrolysis studies: One study (Brightwell and Malik, 00108192) was reviewed and considered scientifically valid and fulfills data requirements by providing information on the hydrolysis of glyphosate and the glyphosate degradate aminomethylphosphonic acid in sterile, buffered water at pH 3, 6, and 9 at 5 and 35 C.

Photodegradation studies in water: No data were submitted, but all data are required.

Photodegradation studies on soil: No data were submitted, but all data are required.

Photodegradation studies in air: No data were submitted, but all data are required.

Aerobic soil metabolism studies: One study (Monsanto Co., 00108140) was reviewed and considered scientifically invalid because the sampling protocol was inadequate to accurately assess the decline of glyphosate and the formation and decline of degradates in soil. In addition, this study would not fulfill data requirements because the study was not run at a constant temperature, complete analytical methods were not reported, complete soil characteristics were not reported, and the test substance was not completely characterized. All data are required.

Anaerobic soil metabolism studies: One study (Monsanto Co., 00108140) was reviewed and is considered scientifically invalid because the sampling protocol was inadequate to accurately assess the decline of glyphosate and the formation and decline of degradates in soil. In addition, this study would not fulfill data requirements because the study was not run at a constant temperature, complete analytical methods were not reported, complete soil characteristics were not reported, and the test substance was not completely characterized. All data are required.

Aerobic aquatic metabolism studies: Two studies were reviewed. One study (Brightwell and Malik, 00108192) is considered scientifically valid; however, this study does not fulfill data requirements because the test waters were not mixed with sediment or soil (Experiment 1), complete water characteristics were not provided, and data on the characterization of radioactivity were not provided for all sampling intervals. The second study (Rueppell, et al., 00108181) is scientifically invalid because the data were too variable to assess the decline of glyphosate and patterns of formation and decline of degradates in water. In addition, this study would not fulfill data requirements because the soil was only sampled at one interval and the water was not characterized. All data are required.

Anaerobic aquatic metabolism studies: One study (Rueppel, et al., 00108181) was reviewed and is scientifically invalid because the data were too variable to assess the decline of glyphosate and patterns of formation and decline of degradates in water. In addition, this study would not fulfill data requirements because the soil was only sampled at one interval, the flooded soil was not aged for 30 days before treatment, and the water was not characterized. All data are required.

Leaching and adsorption/desorption studies: Six studies were reviewed. Two studies (Henshall and Brightwell, 00039943; Edwards, 00039381-C) could not be considered scientifically valid because pretreatment and immediate posttreatment soil samples were not analyzed to confirm glyphosate application rates. In addition, these studies would not fulfill data requirements because the method was not one of the three (i.e., soil TLC, soil columns, batch equilibrium) recommended for determining pesticide mobility in soils, and complete soil characteristics were not presented, and the formulation of the test substance was not reported (00039381-C). Two studies (Monsanto Co., 00108140; Sprankle, et al., 00076493) were considered scientifically valid but neither fulfills data requirements because complete soil characteristics were not reported, the test substance was not characterized, the study was not conducted in a calcium ion solution, incubation conditions were not specified (00108140), K_d values were not reported, desorption of glyphosate was not assessed (00076493), and the test substance was not completely characterized (00076493). The remaining two studies (Brightwell and Malik, 00108192) are valid and partially fulfill data requirements by providing information on the adsorption/desorption of glyphosate in silty clay loam, silt, and two sandy loam soils; and on the mobility of glyphosate (unaged) in sand, silt, clay, sandy clay loam, silty clay loam, and two sandy loam soils and on the mobility of glyphosate residues (aged) in silt, clay, and sandy clay loam soils. In order to fulfill data requirements, complete characteristics for the Cattail Swamp sediment used in the adsorption/desorption experiment in 00108192 or an additional adsorption/desorption experiment using a representative sediment must be submitted.

Laboratory volatility studies: No data were submitted, but all data are required.

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Field volatility studies: No data were submitted; however, the requirement for data is deferred pending the receipt of laboratory volatility data.

Terrestrial field dissipation studies: No data were submitted, but all data are required.

Aquatic field dissipation studies: Six studies were reviewed and two are scientifically valid. The first study (Kramer and Blackburn, 00101561) is scientifically invalid because the analytical methods were inadequate to accurately assess the decline of glyphosate in an aquatic environment. In addition, this study would not fulfill data requirements because the test substance was not completely characterized, complete field test data were not reported, the patterns of formation and decline of degradates other than aminomethylphosphonic acid were not addressed, the sediment was not characterized, the analytical methodology was not reported, and more than one compound was applied to the pond. The second study (Dubelman and Steinmetz, 00077238) is scientifically invalid because the sampling protocol was inadequate to accurately assess the dissipation of glyphosate and the pattern of formation and decline of degradates in water. In addition, this study would not fulfill data requirements because the test substance was not characterized, complete field test data were not reported, sediments were not sampled or characterized, and the patterns of formation and decline of degradates other than aminoethylphosphonic acid were not addressed. The third study (Monsanto Co., 00108140) is scientifically invalid because the test duration and the sampling protocol were inadequate to accurately assess the dissipation of glyphosate and the patterns of formation and decline of degradates in water. In addition, this study would not fulfill data requirements because the test substance was not characterized and soil and sediment samples were not taken. The fourth study (Comes, 00039381) is scientifically invalid because the recovery of glyphosate from fortified water samples was too variable to accurately assess the dissipation of glyphosate from flowing irrigation canal water. In addition, this study would not fulfill data requirements because the test substance was not characterized, soil samples were not analyzed, complete field test data were not reported, and the formation and decline of degradates other than aminomethylphosphonic acid was not addressed. The fifth study (Kramer, 00039381-C) is scientifically valid but does not ful-

fill data requirements because the test substance was not characterized, soil samples were not characterized, complete water characteristics were not reported, rainfall data were not presented, and the formation and decline of degradates other than aminomethylphosphonic acid was not addressed. The sixth study (Blackburn, 00039381-E) is scientifically valid but does not fulfill data requirements because pond water and sediment were not characterized, the pattern of formation and decline of the degradate aminomethylphosphonic acid could not be determined because the data were illegible, more than one pesticide was applied to the test site and may have affected the dissipation of glyphosate from water, and the pattern of formation and decline of degradates other than aminomethylphosphonic acid was not addressed. All data are required.

Forestry dissipation studies: One study (Danhaus, et al., 00093922; Edwards, 00084657) was reviewed and considered to be scientifically valid. This study does not fulfill data requirements because complete soil characteristics were not presented, complete field test data were not reported, the test substance was not characterized, and the duration of the study was inadequate to assess the decline of glyphosate and patterns of formation and decline of degradates in a forest ecosystem. All data are required.

Dissipation studies for combination products and tank mix uses: Five studies were reviewed and three are scientifically invalid. In the first study, three hardcopies (Monsanto Co., 00108176; Ballantine and Herman, 00017701; Schnappinger, 00017706) were combined into one review because they contain data on the same dissipation study. Hardcopies 00108176 and 00017701 contained the analytical method and meteorological data, respectively, for the dissipation study presented in hardcopy 00017706. This study and two others (Schnappinger, 00017703; Kern and Staniforth, 00010704) are scientifically invalid because the data were too variable to accurately assess the dissipation of glyphosate from soil when applied alone or in combination tank mixes. The remaining two studies (Monsanto Co., 00037690; Monsanto Co., 00023979) could not be validated because the analytical methods were not described. No data are required because currently data requirements for combination products and tank mix uses are not being imposed for this Standard.

Long-term field dissipation studies: No data were submitted, but all data may be required based on the results from aerobic soil metabolism/terrestrial field dissipation studies.

Confined accumulation studies on rotational crops: One study (Rueppel, et al., 00108182; Henshall, et al., 00108183) was reviewed and considered scientifically valid. This study does not fulfill data requirements because the plant growth and growing conditions were not completely described and glyphosate residues in the soybeans and the soils were not characterized. All data are required.

Field accumulation studies on rotational crops: No data were submitted; however, the requirement for data is deferred pending receipt of data for confined accumulation studies on rotational crops.

Accumulation studies on irrigated crops: No data were submitted, but all data are required.

Laboratory studies on pesticide accumulation in fish: Five studies were reviewed; two are scientifically valid. The first valid study (Monsanto Co., 00108173-A) does not fulfill data requirements because a flow-through exposure system was not used; [^{14}C]glyphosate residues in soil, water, and test organisms were not characterized; residues in whole fish were not determined; and the test substance was aged. The second valid study (Monsanto Co., 00108173-E) does not fulfill data requirements because radioactive residues were not characterized, radioactive residues in visceral and edible tissue were not analyzed, a flow-through exposure system was not used, and the experiment was not conducted using fish. The third study (Sleight, 00039381-C) could not be validated because insufficient data were presented to support the reported results. In addition, this study would not fullfill data requirements because the purity of the test substance was not reported, radioactive residues were not characterized, cumulative fish mortality was not reported, and radioactive residues in viscera, whole-body tissue, and exposure water, were not provided. The fourth study (Monsanto Co., 00108173) is scientifically invalid because the sampling protocol was inadequate to assess the accumulation of glyphosate in fish. In addition, this study would not fulfill data requirements because a flow-through exposure system was not used, the test organisms were incompletely

described, and the accumulation period was not long enough. The remaining study (Monsanto Co., 00108173-C) is scientifically invalid because the experimental design was inappropriate to assess the accumulation of glyphosate in fish. In addition, this study would not fulfill data requirements because the test substance was not characterized, and data were not reported for the water samples. All data are required.

Field accumulation studies on aquatic nontarget organisms: No data were submitted; however, no data will be required unless data in the laboratory fish accumulation study demonstrate accumulation of glyphosate by fish.

Reentry studies: No data were submitted and no data are required because of the low toxicity and exposure (use) pattern.

Label Restrictions

Pending the submission of rotational crop data do not use ~~pendimethalin~~ glyphosate on rice fields in which crayfish and catfish farming included in the cultural practice, and do not plant crops other than those with registered pendimethalin uses for food or feed in pendimethalin-treated soil.

Pending the submission of irrigated crop data do not use water containing ~~pendimethalin~~ glyphosate residues from rice cultivation to irrigate crops used for food or feed which are not registered for use with ~~pendimethalin~~ glyphosate

References (Studies Reviewed by the Dynamac Corporation)

Ballantine, L.G., and M.M. Herman. 1979. Bicep plus Roundup or paraquat and Dual/Princep plus Roundup or Paraquat tank mix soil dissipation studies: Report No. ABR-79101. Summary of studies 232193-J, 232193-K, 241545-K, 241545-L and 241545-N. (00017701)

Blackburn, R.D. 1975. Dissipation of glyphoste from pond water. In Determination of residues of glyphosate and its metabolite in aquatic use of Roundup herbicide. (00039381-E)

Brightwell, B., and J. Malik. 1978. Solubility, volatility, adsorption and partition coefficients, leaching, and aquatic metabolism of MON 0573 and MON 0101: Report No. MSL-0207. (00108192)

Comes, R.D. 1975. Residues and persistence of glyphosate in irrigation water. In Determination of residues of glyphosate and its metabolite in aquatic use

use of Roundup herbicide. (00039381-D)

Danhaus, R.G., C.M. Lottman, and J.R. Steinmetz, et al. 1979. Roundup Forest Ecosystem: Part II: Residues of glyphosate, aminomethylphosphonic acid and N-nitrosoglyphosate in forest foliage and litter and on mylar spray interceptors, following aerial application of Roundup herbicide: MSL-1974. (00093922)

Dubelman, S., and J.R. Steinmetz. 1981. Glyphosate residues in water following application of Roundup herbicide to flowing bodies of water: MSL-1486. Final rept. Includes method dated Sep. 4, 1980. (00077238)

Edwards, W.M. 1975. Field runoff of glyphosate from Coshocton watersheds. In Determination of residues of glyphosate and its metabolite in aquatic use of Roundup herbicide. (00039381-C)

Edwards, G.A. 1981. Roundup herbicide forest ecosystem study: Part I: Residues of glyphosate, aminomethylphosphonic acid and N-nitrosoglyphosate in forest soil and water following aerial application of Roundup herbicide: Special Report MSL-1830. (00084657)

Henshall, A. and B.B. Brightwell. 1972. Final report on MON-0573, residue and metabolism; Part 7: Runoff of MON-0573 from inclined soil beds. Agricultural Research Report No. 275. (00039943)

Henshall, A., B. Brightwell, and J. Marvel. 1972. Final Report On MON-0573, residue and metabolism: Part 5. Soil binding and phytotoxicity of MON-0573 and its metabolites on soils: Agricultural Research Report No. 274. (00108183)

Kern, C.L. and D. Staniforth. 1978. Metolachlor (Dual 8E) + atrazine (AAtrex) + Glyphosate (Roundup 4E): AG-A No. 4780 I-II. (00010704)

Kramer, R., and R. Blackburn. 1974. Glyphosate dissipation--pond test. (00101561)

Kramer, R.M. 1975. Residues and persistence of glyphosate applied to a dry

irrigation ditch. In Determination of residues of glyphosate and its metabolite in aquatic use of Roundup herbicide. (00039381-A)

Monsanto Co. 1975. Residue and metabolism studies in sugarcane and soils. (00108140)

Monsanto Co. 1975. Residue studies and methods of analysis for preemergent use of glyphosate in cotton. (00108176)

Monsanto Co. 1978. Residue studies for use of Roundup herbicide in aquatic situations. (00108173)

Monsanto Co. 1978. Residue studies for use of roundup herbicide in aquatic situations. (00108173-A)

Monsanto Co. 1978. Residue studies for use of Roundup herbicide in aquatic situations. (00108173-C)

Monsanto Co. 1978. Residues for use of Roundup herbicide in Aquatic Situations. (00108173-E)

Monsanto Company. 19??. The soil dissipation of glyphosate, alachlor and simazine herbicides. (00023979)

Monsanto Company. 19??. Soil dissipation of Roundup, Lasso and cyanazine herbicides. (00037690)

Rueppel, M., B. Brightwell, and A. Henshall, et al. 1972. Final Report on MON-0573, residue and metabolism: Part 4. The rate of dissipation of MON-0573 in soil: Agricultural Research Report No. 271. (00108182)

Rueppel, M., B. Brightwell, and J. Marvel, et al. 1972. Final Report on MON-0573, residue and metabolism: Part 3. The degradation and metabolism of MON-0573 in soil: Agricultural Research Report No. 269. (00108181)

Schnappinger, M.G. 1979. Metolachlor (Dual 8E); simazine (Princep 4L); paraquat (paraquat 2CL); glyphosate (Roundup 4E): AG-A No. 6061 I-VII. (00017706)

Schnappinger, M.G. 1978. Metolachlor (Dual 8E) + Atrazine (AAtrex 80 W) + Glyphosate (Roundup 4E): AG-A No. 4597 I-IV. (00017703)

Sleight III, B.H. 1975. Exposure of fish to Roundup, accumulation, distribution, and elimination. In Determination of residues of glyphosate and its metabolite in aquatic use of Roundup herbicide. (00039381-C)

Sprankle, P., D. Penner, and W.F. Meggitt. 1973. Adsorption and degradation of Glyphosate in the soil. (00076493)

DYNAMAC
CORPORATION

GLYPHOSATE

Final Report

Task 1: Review and Evaluation of Individual Studies

Contract No. 68-01-6679

JUNE 3, 1985

Submitted to:
Environmental Protection Agency
Arlington, VA 22202

Submitted by:
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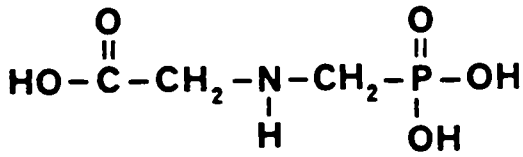
Enviro Control Division
The Dynamac Building
11140 Rockville Pike
Rockville, MD 20852

GLYPHOSATE

ROUNDUP



N-(phosphonomethyl)glycine

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Study

8 Brightwell, B., and J. Malik. 1978. Solubility, volatility, adsorption and partition coefficients, leaching, and aquatic metabolism of MON 0573 and MON 0101: Report No. MSL-0207. (00108192)

9 Danhaus, R.G., C.M. Lottman, and J.R. Steinmetz, et al. 1979. Roundup Forest Ecosystem: Part II: Residues of glyphosate, aminomethylphosphonic acid and N-nitrosoglyphosate in forest foliage and litter and on mylar spray interceptors, following aerial application of Roundup herbicide: MSL-1974. (00093922)

Edwards, G.A. 1981. Roundup herbicide forest ecosystem study: Part I: Residues of glyphosate, aminomethylphosphonic acid and N-nitrosoglyphosate in forest soil and water following aerial application of Roundup herbicide: Special Report MSL-1830. (00084657)

10 Kramer, R., and R. Blackburn. 1974. Glyphosate dissipation--pond test. (00101561)

11 Monsanto Co. 1975. Residue studies and methods of analysis for preemergent use of glyphosate in cotton. (00108176)

Ballantine, L.G., and M.M. Herman. 1979. Bicep plus Roundup or paraquat and Dual/Princep plus Roundup or Paraquat tank mix soil dissipation studies: Report No. ABR-79101. Summary of studies 232193-J, 232193-K, 241545-K, 241545-L and 241545-N. (00017701)

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12 Schnappinger, M.G. 1978. Metolachlor (Dual 8E) + Atrazine (AAtrex 80 W) + Glyphosate (Roundup 4E): AG-A No. 4597 I-IV. (00017703)

13 Monsanto Company. 19??. Soil dissipation of Roundup, Lasso and cyanazine herbicides. (00037690)

14 Kramer, R.M. 1975. Residues and persistence of glyphosate applied to a dry irrigation ditch. In Determination of residues of glyphosate and its metabolite in aquatic use of Roundup herbicide. (00039381-A)

15 Monsanto Company. 19??. The soil dissipation of glyphosate, alachlor and simazine herbicides. (00023979)

16 Kern, C.L. and D. Staniforth. 1978. Metolachlor (Dual 8E) + atrazine (AAtrex) + Glyphosate (Roundup 4E): AG-A No. 4780 I-II. (00010704)

17 Edwards, W.M. 1975. Field runoff of glyphosate from Coshocton watersheds. In Determination of residues of glyphosate and its metabolite in aquatic use of Roundup herbicide. (00039381-C)

Table of Contents (Continued)

Study

CASE GS0178 GLYPHOSATE STUDY 1 PM 25 06/16/83

CHEM 103601 Isopropylamine glyphosate

BRANCH EFB DISC 30 TOPIC 050530 GUIDELINE 40 CFR 163.62-10b

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00108182 CONTENT CAT 01

Rueppel, M., B. Brightwell, and A. Henshall, et al. 1972. Final Report on MON-0573, residue and metabolism: Part 4. The rate of dissipation of MON-0573 in soil: Agricultural Research Report No. 271. Unpublished study received Jan. 30, 1973 under unknown admin. no.; submitted by Monsanto Co., Washington, DC; CDL:120303-E.

FICHE/MASTER ID 00108183 CONTENT CAT 01

Henshall, A., B. Brightwell, and J. Marvel. 1972. Final Report On MON-0573, residue and metabolism: Part 5. Soil binding and phytotoxicity of MON-0573 and its metabolites on soils: Agricultural Research Report No. 274. Unpublished study received Jan. 30, 1973 under unknown admin. no.; submitted by Monsanto Co., Washington, DC; CDL:120303-F.

SUBST. CLASS = S.

DIRECT RVW TIME = 22 (MH) START-DATE END DATE

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Two hardcopies (00108182, 00108183) were combined for this review because they describe a single greenhouse study.

CONCLUSIONS:

Confined Accumulation - Rotational Crops

1. This study is scientifically valid.

2. [^{14}C]Glyphosate residues in 4-week-old soybeans grown in aged (16-weeks) water-extracted and unextracted silt, sandy loam, and silty clay loam soils treated with [^{14}C]glyphosate (purity ~96%) at 4 ppm ranged from 0.76 to 4.12 ppb. Glyphosate residues in the soil during the growing period ranged from 0.64 to 3.72 ppm.

3. This study does not fulfill EPA Data Requirements for Registering Pesticides because the plant growth and growing conditions were not completely described and glyphosate residues in the soybeans and the soils were not characterized.

MATERIALS AND METHODS:

Three soils (Table 1) were adjusted to 11% moisture and treated with methyl-labeled [^{14}C]glyphosate (MON 0543, ~96% pure, specific activity 8.03 mCi/mM, Monsanto Corporation) at 4 ppm. The treated soils were planted with corn and aerobically incubated (90 F) for 16 weeks in the greenhouse. Following the incubation, half of each treated soil (~1 kg) was lyophilized and sieved; the remaining soil (~1 kg) was extracted 5 times with water, lyophilized and sieved. Both soils were placed in plastic pots, planted with soybeans, watered, and incubated in the greenhouse at 75 F. After seed germination, the pots were watered twice daily. The plant shoots were harvested after 4 weeks, ground, and analyzed for total radioactivity by combustion and LSC.

Soil samples were taken immediately after treatment, before planting the soybeans, and after harvest and analyzed for total radioactivity by combustion and LSC.

REPORTED RESULTS:

[^{14}C]Glyphosate residues in soybeans grown in unextracted soil totaled 0.096%, 0.019%, and 0.051% of the applied radioactivity for the silt, sandy loam, and silty clay loam soils, respectively (Table 2). Residues in soybeans grown in water-extracted soil totaled 0.103%, 0.071%, and 0.039% of the applied radioactivity for the silt, sandy loam, and silty clay loam soils, respectively.

DISCUSSION:

1. Plant growth and growing conditions were not adequately described (watering, growth rate, and soil temperature).

2. Residues in the soil and plants were not characterized.

3. No CEC data were reported. The reported soil textures could not be verified because the sums of the fractions did not total 100%. Based on the reported fractions, the soil reported to be a silt loam would be a silt, and the soil reported to be sandy loam would be a loamy sand according to the USDA soil classification system.

4. Detections limits and percent recovery from fortified samples were not reported.

Table 1. Soil characteristics.

Soil type	pH	Sand	Silt	Clay	Organic matter
		%			
Silt	6.5	6.0	83.2	9.6	1.0
Silty clay loam	7.0	2.0	55.4	36.8	6.0
Loamy sand	5.7	86.0	11.0	2.3	1.0

Table 2. [^{14}C]Glyphosate residues (% of applied) in soybeans grown on water-extracted and unextracted soil and in soils treated at 4 ppm and aged for 112 days.

Soil type	Soil			
	Posttreatment[a]	Preplant[b]	Final	Plant
Silt	97.7			
Unextracted		21.9	19.4	0.096
Extracted		17.1	18.2	0.103
Sandy loam	97.8			
Unextracted		92.9	91.1	0.019
Extracted		56.3	57.6	0.071
Silty clay loam	94.2			
Unextracted		43.0	36.6	0.051
Extracted		35.5	31.4	0.039

[a] Immediate posttreatment samples; values represent extractable plus soil bound residues recovered.

[b] Values represent the % of applied radioactivity detected after aging for 112 days, immediately before planting to soybeans.

CASE GS0178 GLYPHOSATE STUDY 2 PM 25 06/16/83

CHEM 103601 Isopropylamine glyphosate

BRANCH EFB DISC 30 TOPIC

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00108181 CONTENT CAT 01

Rueppel, M., B. Brightwell, and J. Marvel, et al. 1972. Final Report on MON-0573, residue and metabolism: Part 3. The degradation and metabolism of MON-0573 in soil: Agricultural Research Report No. 269. Unpublished study received Jan. 30, 1973 under unknown admin. no.; submitted by Monsanto Co., Washington, DC; CDL:120303-D.

SUBST. CLASS = S.

DIRECT RVW TIME = 19 (MH) START-DATE END DATE

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CONCLUSIONS:

Metabolism - Aerobic Aquatic

This portion of the study is scientifically invalid because the data were too variable to assess the decline of glyphosate and patterns of formation and decline of degradates in water. In addition, this portion of the study would not fulfill EPA Data Requirements for Registering Pesticides because the soil was only sampled at one interval and the water was not characterized.

Metabolism - Anaerobic Aquatic

This portion of the study is scientifically invalid because the data were too variable to assess the decline of glyphosate and patterns of formation and decline of degradates in water. In addition, this portion of the study would not fulfill EPA Data Requirements for Registering Pesticides because

the soil was only sampled at one interval, the flooded soil was not aged for 30 days before treatment, and the water was not characterized.

MATERIALS AND METHODS:

Metabolism - Aerobic Aquatic

Samples (5.0 g) of four soils (Table 1) were placed in flasks with 100 ml of distilled water and treated with methyl-labeled, 1-glycine-labeled, or 2-glycine-labeled [^{14}C]glyphosate (specific activity 8.06-10.02 mCi/mM, >96% pure, Monsanto Corporation) at ~10.0 ppm. The flasks were incubated on a shaker, at 30 C for 28, 35, 84, and 112 days, for the Ray, Lintonia, Drummer and Norfolk soils, respectively.

Radioactivity evolved as $^{14}CO_2$ was collected in ascarite traps by purging the flasks with air. Radioactivity was removed from the ascarite by acidification and quantified by LSC. Samples of the supernatant were taken at 14 and 28 days (Ray silt loam); 14, 28, 56, and 112 days (Norfolk sandy loam); 14, 28, 56, and 84 days (Drummer silty clay loam); and 14 and 35 days (Lintonia sandy loam). The supernatant was spotted on TLC plates and developed two dimensionally with eluant I (84 ml aqueous phenol:16 ml water:37.2 g disodium EDTA:1.0 ml acetic acid) followed by eluant II (1.2 g disodium EDTA:100 ml 17N ammonium hydroxide:475 ml water:350 ml 1-propanol:75 ml 2-propanol:75 ml 1-butanol:2.5 l isobutyric acid). Radioactivity was quantified by beta analysis. Soil samples, taken at day 28, 35, 84, and 112 days for the Ray, Lintonia, Drummer and Norfolk soils respectively, were extracted with water, centrifuged, and lyophilized. Total radioactivity in subsamples was determined by combustion and LSC. The remaining sample was extracted 3 times with 0.5 N ammonium hydroxide, and the extracts (water and ammonium hydroxide) were analyzed by TLC/beta camera analysis. Nonextractable radioactivity in the extracted soil samples was determined by combustion and LSC. Recovery values were 76.3, 95.9 and 100% from the Drummer, Ray and Norfolk soils, respectively.

Metabolism - Anaerobic Aquatic

Sample flasks with identical soil samples as in Metabolism- Aerobic Aquatic (treated with [^{14}C]glyphosate and incubated as described previously) were purged with nitrogen gas and the radioactivity evolved as $^{14}CO_2$ was collected and quantified. Supernatant and soil samples were collected and quantified as previously described.

REPORTED RESULTS:

Metabolism - Aerobic Aquatic

The radioactivity detected in aerobically incubated flooded soil is shown in Table 2. Parent glyphosate and degradates detected in the soil extracts and the water are shown in Table 3 and 4. The data presented for all soils and water were variable.

Metabolism - Anaerobic Aquatic

The radioactivity detected in anaerobically incubated flooded soil is shown in Table 5. Parent glyphosate and degradates detected in the soil and supernatant are shown in Tables 6 and 7, respectively. The data presented for all soils and water were variable.

DISCUSSION:

General - Both Experiments

1. Soil samples were analyzed only at the end of the study. Consequently, the pattern of decline of glyphosate and patterns of formation and decline of degradates in the flooded soils could not be determined.

2. The soil textural classes could not be verified for all soils because the sum of the sand, silt, and clay fractions did not total 100%. Based on the percentages reported, the Drummer silty clay loam and the Norfolk sandy loam would be a silty clay and a loamy sand, respectively according to the USDA Soil Textural Classification System.

3. Detection limits were not reported.

4. It was not clear whether the test substance was added before or after flooding.

5. The water was not characterized.

Metabolism - Anaerobic Aquatic

The soil was not flooded for 30 days prior to treatment with [^{14}C]glyphosate.

Table 1. Soil characteristics.

Soil type	Sand	Silt	Clay	Organic matter	pH
		%			
Ray silt loam	6.0	82.3	0.6	1.0	6.5
Drummer silty clay	2.0	55.4	36.8	6.0	7.0
Lintonia sandy loam	70.0	21.0	9.0	1.0	6.0
Norfolk loamy sand	86.0	11.0	2.3	1.0	5.7

Table 2. Radioactivity (% of applied) detected in four flooded soils[a] treated with [^{14}C]glyphosate at 10 ppm and aerobically incubated, with shaking, at 30 C.

Test substance	$^{14}CO_2$	Water soluble		Soil		Total recovered
		Supernatant	Soil wash	Extractable	Nonextractable	
			Ray silt loam			
1-methyl-labeled [^{14}C]glyphosate	46.8	5.4	1.6	22.9	8.5	85.2
1-glycine-labeled [^{14}C]glyphosate	55.3	0.3	0.1	2.7	9.7	68.1
2-glycine-labeled [^{14}C]glyphosate	55.3	1.4	0.1	6.4	40.3	103.5
			Drummer silty clay			
1-methyl-labeled [^{14}C]glyphosate	34.7	18.1	6.9	19.6	16.7	96.0
1-glycine-labeled [^{14}C]glyphosate	41.4	15.9	8.7	13.0	18.0	97.0
2-glycine-labeled [^{14}C]glyphosate	38.3	8.4	5.3	12.0	33.9	97.9
			Norfolk loamy sand			
1-methyl-labeled [^{14}C]glyphosate	5.8	0.8	0.6	81.8	10.5	99.5
1-glycine-labeled [^{14}C]glyphosate	9.3	16.3	6.0	65.4	4.6	101.6
2-glycine-labeled [^{14}C]glyphosate	8.5	2.4	4.1	81.3	13.5	109.8
			Lintonia sandy loam			
1-methyl-labeled [^{14}C]glyphosate	14.2	66.1	2.0	18.3	2.6	103.5

[a] Ray silt loam samples were analyzed after 28 days; Drummer silty clay samples were analyzed after 84 days; Norfolk loamy sand samples were analyzed after 112 days; Lintonia sandy loam samples were analyzed after 35 days.

Table 3. [^{14}C]Glyphosate and AMPA[a] (% of applied) detected in four flooded soils[b] treated at 10 ppm and aerobically incubated with shaking at 30 C.

Test substance	Glyphosate	AMPA	Other
	Ray silt loam		
1-methyl-labeled [^{14}C]glyphosate	1.5	21.2	0.2
1-glycine-labeled [^{14}C]glyphosate	1.7	ND	1.0
2-glycine-labeled [^{14}C]glyphosate	1.1	ND	5.3
	Drummer silty clay		
1-methyl-labeled [^{14}C]glyphosate	12.0	7.1	0.5
1-glycine-labeled [^{14}C]glyphosate	12.7	ND	0.3
2-glycine-labeled [^{14}C]glyphosate	9.9	ND	2.2
	Norfolk loamy sand		
1-methyl-labeled [^{14}C]glyphosate	71.4	6.6	4.7
1-glycine-labeled [^{14}C]glyphosate	63.5	ND	2.0
2-glycine-labeled [^{14}C]glyphosate	79.2	ND	2.2
	Lintonia sandy loam		
1-methyl-labeled [^{14}C]glyphosate	13.6	4.9	ND

[a] Aminomethylphosphonic acid.

[b] Ray silt loam samples were analyzed after 28 days; Drummer silty clay samples were analyzed after 84 days; Norfolk loamy sand samples were analyzed after 112 days; Lintonia sandy loam samples were analyzed after 35 days.

Table 4. [^{14}C]Glyphosate and AMPA[a] detected (% of applied) in supernatant from shake flasks treated with [^{14}C]glyphosate at 10 ppm and incubated aerobically at 30 C.

Test substance	Sampling interval (days)	Glyphosate	AMPA	Other
	Ray silt loam			
1-methyl-labeled [^{14}C]glyphosate	14	0.2	8.5	0.6
	28	ND[b]	4.4	1.0
1-glycine-labeled [^{14}C]glyphosate	14	0.7	ND	ND
	28	ND	ND	ND
2-glycine-labeled [^{14}C]glyphosate	14	7.4	ND	2.7
	28	ND	ND	ND
	Drummer silty clay			
1-methyl-labeled [^{14}C]glyphosate	14	12.5	1.8	0.3
	28	13.7	5.6	1.1
	56	13.4	8.4	2.1
	84	7.6	8.3	2.1
1-glycine-labeled [^{14}C]glyphosate	14	17.5	ND	ND
	28	20.9	ND	0.8
	56	20.8	ND	1.0
	84	15.7	ND	0.2
2-glycine-labeled [^{14}C]glyphosate	14	25.5	ND	ND
	28	14.0	ND	0.4
	56	16.1	ND	0.6
	84	8.3	ND	0.1
	Norfolk loamy sand			
1-methyl-labeled [^{14}C]glyphosate	14	45.6	0.5	ND
	28	65.2	1.7	ND
	56	28.1	ND	ND
	112	0.8	ND	ND
1-glycine-labeled [^{14}C]glyphosate	14	48.3	ND	ND
	28	76.3	ND	ND
	56	72.6	ND	ND
	112	16.3	ND	ND
2-glycine-labeled [^{14}C]glyphosate	14	80.1	ND	ND
	28	77.6	ND	ND
	56	57.6	ND	ND
	112	2.2	ND	0.2
	Lintonia sandy loam			
1-methyl-labeled [^{14}C]glyphosate	14	69.5	6.9	ND
	35	59.5	6.6	ND

[a] Aminomethylphosphonic acid.

[b] Not detected; detection limit not reported.

Table 5. Radioactivity (% of applied) detected in four flooded soils[a] treated with [^{14}C]glyphosate at 10 ppm and anaerobically incubated, with shaking at 30 C.

Test substance	$^{14}CO_2$	Water soluble		Soil		Total recovered
		Supernatant	Soil wash	Extractable	Nonextractable	
			Ray silt loam			
1-methyl-labeled [^{14}C]glyphosate	37.1	2.6	0.3	33.5	12.8	86.3
1-glycine-labeled [^{14}C]glyphosate	51.4	0.2	0.1	4.1	14.1	69.9
2-glycine-labeled [^{14}C]glyphosate	33.5	4.8	0.2	7.5	29.7	75.7
			Drummer silty clay			
1-methyl-labeled [^{14}C]glyphosate	25.1	18.8	4.2	15.3	15.1	78.5
1-glycine-labeled [^{14}C]glyphosate	38.6	8.1	0.8	3.3	15.6	66.4
2-glycine-labeled [^{14}C]glyphosate	24.2	16.1	2.9	15.5	31.6	90.3
			Norfolk loamy sand			
1-methyl-labeled [^{14}C]glyphosate	2.4	1.7	0.8	92.2	12.0	109.1
1-glycine-labeled [^{14}C]glyphosate	5.0	64.2	7.9	26.7	2.4	101.2
2-glycine-labeled [^{14}C]glyphosate	1.4	89.9	2.3	0.5	0.4	94.5
			Lintonia sandy loam			
1-methyl-labeled [^{14}C]glyphosate	6.0	60.9	3.9	28.8	6.5	106.7

[a] Ray silt loam samples were analyzed after 28 days; Drummer silty clay samples were analyzed after 84 days; Norfolk loamy sand samples were analyzed after 112 days; Lintonia sandy loam samples were analyzed after 35 days.

Table 6. [^{14}C]Glyphosate and AMPA[a] (% of applied) detected in four flooded soils[b] treated at 10 ppm and anaerobically incubated with shaking at 30 C.

Test substance	Glyphosate	AMPA	Other
	Ray silt loam		
1-methyl-labeled [^{14}C]glyphosate	3.0	29.7	0.9
1-glycine-labeled [^{14}C]glyphosate	2.4	ND	1.7
2-glycine-labeled [^{14}C]glyphosate	1.7	ND	5.9
	Drummer silty clay		
1-methyl-labeled [^{14}C]glyphosate	3.3	12.0	4.9
1-glycine-labeled [^{14}C]glyphosate	2.8	ND	0.5
2-glycine-labeled [^{14}C]glyphosate	11.8	ND	3.5
	Norfolk loamy sand		
1-methyl-labeled [^{14}C]glyphosate	81.2	6.1	4.9
1-glycine-labeled [^{14}C]glyphosate	21.7	ND	ND
2-glycine-labeled [^{14}C]glyphosate	ND	ND	ND
	Lintonia sandy loam		
1-methyl-labeled [^{14}C]glyphosate	27.2	2.2	ND

[a] Aminomethylphosphonic acid

[a] Ray silt loam samples were analyzed after 28 days; Drummer silty clay samples were analyzed after 84 days; Norfolk loamy sand samples were analyzed after 112 days; Lintonia sandy loam samples were analyzed after 35 days.

Table 7. [^{14}C]Glyphosate and AMPA[a] detected (% of applied radioactivity) in supernatant from shake flasks treated with [^{14}C]glyphosate at 10 ppm and incubated anaerobically at 30 C.

Test substance	Sampling interval (days)	Glyphosate	AMPA[a]	Other
		Ray silt loam		
1-methyl-labeled [^{14}C]glyphosate	14	0.5	12.9	0.6
	28	ND[b]	1.9	0.6
1-glycine-labeled [^{14}C]glyphosate	14	0.9	ND	ND
	28	ND	ND	ND
2-glycine-labeled [^{14}C]glyphosate	14	2.2	ND	0.7
	28	ND	ND	ND
		Drummer silty clay		
1-methyl-labeled [^{14}C]glyphosate	14	16.0	7.2	0.3
	28	2.3	14.8	1.1
	56	1.3	13.5	2.1
	84	1.0	15.0	2.1
1-glycine-labeled [^{14}C]glyphosate	14	18.0	ND	0.1
	28	14.0	ND	0.2
	56	6.8	ND	0.5
	84	8.1	ND	ND
2-glycine-labeled [^{14}C]glyphosate	14	30.8	ND	ND
	28	20.3	ND	0.4
	56	16.5	ND	0.2
	84	15.2	ND	1.0
		Norfolk loamy sand		
1-methyl-labeled [^{14}C]glyphosate	14	77.3	ND	ND
	28	66.1	1.1	ND
	56	71.5	1.1	ND
	112	1.7	ND	ND
1-glycine-labeled [^{14}C]glyphosate	14	82.5	ND	ND
	28	73.9	ND	0.2
	56	82.1	ND	0.7
	112	63.9	ND	0.1
1-glycine-labeled [^{14}C]glyphosate	14	82.5	ND	ND
	28	73.9	ND	0.2
	56	82.1	ND	0.7
	112	63.9	ND	0.1
2-glycine-labeled [^{14}C]glyphosate	14	90.7	ND	ND
	28	99.5	ND	0.3
	56	103.3	ND	0.5
	112	82.9	ND	0.7
		Lintonia sandy loam		
1-methyl-labeled [^{14}C]glyphosate	14	82.9	3.9	ND
	35	58.2	2.7	ND

[a] Aminomethylphosphonic acid.

[b] Not detected; detection limit not reported.

CASE GS0178 GLYPHOSATE STUDY 3 PM 25 06/16/83

CHEM 103601 Isopropylamine glyphosate

BRANCH EFB DISC 30 TOPIC

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00039943 CONTENT CAT 01

Henshall, A. and B.B. Brightwell. 1972. Final report on MON-0573, residue and metabolism; Part 7: Runoff of MON-0573 from inclined soil beds. Agricultural Research Report No. 275.

SUBST. CLASS = S.

DIRECT RVW TIME = 9 1/2 (MH) START-DATE END DATE

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CONCLUSION:

Mobility - Leaching and Adsorption/Desorption

This runoff study could not be validated because pretreatment and immediate posttreatment soil samples were not analyzed to confirm glyphosate application rates. In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides because the method was not one of the three (i.e., soil TLC, soil columns, batch equilibrium) recommended for determining pesticide mobility in soils, and complete soil characteristics were not presented.

MATERIALS AND METHODS:

Soil beds (stainless steel, 36-inch length x 12-inch width x 6-inch depth, 7.5° slope) were filled to a 5 inch depth with Ray silt loam, Norfolk sandy loam, or Drummer silty clay loam soil (Table 1). [^{14}C]-Glyphosate (MON 0573, ~93% pure, specific activity 8.32 mCi/mM, source unspecified) in 0.1 M ammonium carbonate, was surface applied at 1.0 lb ai/A to the upper third of the soil bed. The soil was watered to saturation at 0.75 inches/hour 1, 3 and 7 days after treatment. Two 50-ml runoff samples were collected sequentially from the soil beds (Table 2).

The runoff samples were centrifuged and aliquots of the water fraction were analyzed for radioactivity by LSC. Sediment samples were lyophilized and analyzed for total radioactivity by combustion and LSC.

REPORTED RESULTS:

A total of 0.0115, 0.0144, and 0.0044% of the applied radioactivity was recovered from runoff water samples from the silt loam, sandy loam, and silty clay loam soils, respectively (Table 3). Radioactivity recovered in the sediment totaled 0.0084% (silt loam), 0.0071% (sandy loam) and 0.00079% (silty clay loam) of applied.

DISCUSSION:

1. Complete soil characteristics, such as CEC and silt and sand content, were not reported.

2. The method was not one of the three (i.e. soil TLC, soil column, or batch equilibrium) recommended for determining pesticide mobility in soils.

3. The detection limit and recoveries from fortified samples were not reported.

4. Soil samples, other than the sediment fraction of the runoff water, were not analyzed for [^{14}C]glyphosate residues. Consequently, vertical or horizontal movement of [^{14}C]glyphosate in the soil could not be determined, and the extent of glyphosate mobility in runoff could not be accurately determined.

5. Total runoff from the soil beds was not reported. The amount of runoff water collected (two 50-ml samples) may not have been adequate to estimate pesticide loss in runoff water.

Table 1. Soil characteristics.

Soil type	Clay %	Organic matter %	pH
Ray silt loam	10	1	6.5
Norfolk sandy loam	2	1	5.7
Drummer silty clay loam	37	6	7.0

Table 2. Water (inches) required[a] to initiate runoff from 3 soils treated with [^{14}C]glyphosate at 1.0 lb ai/A.

Soil type	Day 1	Day 3	Day 7	Total applied
Silt loam	0.75	0.15	0.21	1.11
Sandy loam	0.91	0.15	0.28	1.34
Silty clay loam	0.43	0.21	0.30	0.94

[a] Water was applied at 0.75 inch/hour.

Table 3. Radioactivity (% of applied) in 50-ml samples of runoff water and sediment from three soils treated with [^{14}C]glyphosate at 1.0 lb. ai/A.

Sampling interval (days)	Silt loam		Sandy loam		Silty clay loam	
	Water	Sediment	Water	Sediment	Water	Sediment
1	0.0028	0.0021	0.0062	0.0030	0.0001	0.00004
	0.0061	0.0016	0.0065	0.0032	0.0002	0.00003
3	0.0009	0.0013	0.0007	0.0003	0.0009	0.0001
	0.0011	0.0018	0.0006	0.0003	0.0016	0.0001
7	0.0003	0.0007	0.0002	0.0001	0.0007	0.00001
	0.0003	0.0009	0.0002	0.0002	0.0009	0.00001
Total	0.0115	0.0084	0.0144	0.0071	0.0044	0.00029

CASE GS0178 GLYPHOSATE STUDY 4 PM 25 06/16/83

CHEM 103601 Isopropylamine glyphosate

BRANCH EFB DISC 30 TOPIC 0505

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00076493 CONTENT CAT 01

Sprankle, P., D. Penner, and W.F. Meggitt. 1973. Adsorption and degradation of Glyphosate in the soil. Unpublished study received Nov. 9, 1973, under 524-308; submitted by Monsanto Co., Washington, D.C.; CDL:120640-E.

SUBST. CLASS = S.

DIRECT RVW TIME = 6 (MH) START-DATE END DATE

REVIEWED BY: G. Moore
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CONCLUSIONS:

Mobility- Leaching and Adsorption/Desorption

1. This study is scientifically valid.
2. Sphinx sandy loam soil, treated with [^{14}C]glyphosate at ~0.1 µCi/g, adsorbed 16.5 nMoles/g of [^{14}C]glyphosate (test substance uncharacterized) during 4 hours of mixing in a 15:1 water:soil slurry. The addition of various concentrations of phosphate to the soil had no discernible effect on glyphosate adsorption.
3. This study does not fulfill EPA Data Requirements for Registering Pesticides because complete soil characteristics were not reported, the test substance was not characterized, the study was not conducted in a calcium ion solution, incubation conditions were not specified, and K_d values were not reported.

MATERIALS AND METHODS:

Three soils were air-dried, sieved to ≤1mm, and treated with phosphate (Table 1). Soil samples (0.4 g) were placed in glass tubes and treated with 6 ml of a [^{14}C]glyphosate (test substance uncharacterized, source unspecified) solution containing ~0.04 µCi of radioactivity. The solutions were mixed on a horizontal shaker for 4 hours and then centrifuged.

Aliquots of the supernatants were analyzed for total radioactivity (analytical method unspecified).

REPORTED RESULTS:

Sphinx sandy loam soil adsorbed the least [^{14}C]glyphosate (16.5 nMoles/g); Conover sandy loam and Toledo clay loam soils adsorbed 22.3-37.6 nMoles/g (Table 1). Phosphate had no observable effect on glyphosate adsorption.

DISCUSSION:

1. The soils were modified by the addition of phosphate, which may have affected the rate of adsorption of glyphosate to soil.

2. Complete soil characteristics, such as CEC and sand and silt content, were not reported.

3. No description of the analytical methods were provided; however, it was assumed that total radioactivity was determined using LSC.

4. The test substance was not characterized.

5. K_d values were not calculated.

6. The application rate, reported as µCi of [^{14}C]glyphosate, was not related to the the results, which were reported on a nanomolar basis. In addition, only one concentration of the pesticide was applied.

7. The study was not conducted in a calcium ion solution.

8. The temperature at which the study was conducted was not specified.

Table 1. Soil characteristics, phosphate application rates, and concentration of [^{14}C]glyphosate adsorbed to soils.

Type	Clay (%)	Organic matter (%)	pH	Phosphate applied (kg/ha)	Glyphosate adsorbed
Sphinx sandy loam	21.7	2.0	6.1	330	16.5
Conover sandy loam	22-30	2.7	6.1	128	36.4
				112	37.6
				76	27.3
Toledo clay loam	70-72	3.8	7.5	249	22.3
				47	34.0
				15	27.1
				9	37.4

CASE GS0178 GLYPHOSATE STUDY 5 PM 25 06/16/83

CHEM 103601 Isopropylamine glyphosate

BRANCH EFB DISC 30 TOPIC 051025 GUIDELINE 40 CFR 163.62-10c

FORMULATION 15 - SOLUBLE CONCENTRATE

FICHE/MASTER ID 00108173-A CONTENT CAT 01

Monsanto Co. 1978. Residue studies for use of roundup herbicide in aquatic situations. Compilation; unpublished study received Dec. 27, 1978 under 524-308; CDL;097764-A; 097761; 097762.

SUBST. CLASS = S.

DIRECT RVW TIME = 14 (MH) START-DATE END DATE

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CONCLUSIONS:

Laboratory Accumulation - Fish

1. The portion of the study pertaining to crayfish is scientifically invalid because the data were too variable to assess the accumulation of glyphosate in crayfish. The portion of the study pertaining to catfish is scientifically valid.

2. [^{14}C]Glyphosate residues (uncharacterized) accumulated in catfish exposed to N-phosphonomethyl-labeled [^{14}C]glyphosate (~98% pure) for 28 days, with a maximum bioconcentration factor of 1.87x and 13.75x in edible and visceral tissue, respectively. Accumulated [^{14}C]glyphosate residues were depurated fairly rapidly with ~76% of the residues detected after 28 days of exposure being eliminated after 28 days in untreated water.

3. This study does not fulfill EPA Data Requirements for Registering Pesticides because a flow-through exposure system was not used; [^{14}C]glyphosate residues in soil, water, and test organisms were not characterized; residues in whole fish were not determined; and the test substance was aged.

MATERIALS AND METHODS:

Spinks sandy loam soil (75% sand, 17.8% silt, 4.8% clay, 2.4% organic matter, pH 4.7) was spread to a depth of 2.5 cm in a circular 2-m diameter metal tank, and treated with N-phosphonomethyl-labeled [^{14}C]glyphosate (~98.6% pure, specific activity 1640 ± 7 dpm/µg, Monsanto Corp.) at 14.3 ppm. A second system, using untreated soil, was similarly prepared to serve as a control. The soils were aerobically aged for 3 days under fluorescent lights (10 hours light, 14 hours dark) after which the tanks were flooded (2.5 cm depth) with 78 l of aerated well water (pH 7.1, total hardness 35 mg/l calcium carbonate) and anaerobically aged for an additional 27 days. After the aging period, the tanks were filled with ~1500 l of aerated well water (water temperature 18 ± 1 C).

After equilibrating for 2 days, 108 channel catfish (Ictalurus punctatus, 100 with an average weight of 4.2 g, average length of 6.3 cm; 8 with an average weight of 24 g, average length, 9.8 cm) and 100 crayfish (Procambas clarki, 24 g average weight, 9.8 cm average length) were introduced into each system. Cumulative mortality for the organisms was <3% during a 30 day acclimation period. Dissolved oxygen was maintained at >55% saturation during the exposure and depuration stages of the experiment.

Soil samples were taken at days 0, 3, 4, 15, and 30 during the aging period and on day 0, 1, 3, 7, 10, 14, 21, and 28 during the exposure period. Water samples were taken at days 1, 12 and 27 after flooding and on days 0, 1, 3, 7, 10, 14, 21, and 28 during exposure. The control tank was sampled at day 0 during the aging period (soil) and on days 1 and 28 during the exposure period (water and soil). Additional water samples were taken at the same intervals, centrifuged, and the supernatant analyzed for total radioactivity in order to quantify glyphosate associated with soil particles in solution. Catfish and crayfish were sampled on days 1, 3, 7, 10, 14, 21, and 28 during exposure. Organisms remaining in the tanks after 28 days of exposure were depurated in untreated water for 28 days (catfish) and 14 days (crayfish) with samples taken on days 1, 3, 7, 10, 14, 21, and 28 and 1, 3, 7, and 14 for catfish and crayfish, respectively.

Soil samples were air-dried and analyzed for total radioactivity by combustion and LSC. Water samples were analyzed for total radioactivity by LSC. Samples of the muscle and visceral tissues were air-dried, combusted, and the radioactivity was quantified by LSC.

In addition, the distribution of polar, non-polar, and non-extractable residues were determined by extracting muscle and viscera tissue samples with hexane and methanol. Radioactivity in the extracts was quantified by LSC. Unextractable radioactivity remaining in the tissue was quantified by combustion and LSC. Recovery values for the total combustion were 99-101% based on standard reference materials. Detection limits for muscle tissue were 0.009 ppm and 0.006 ppm for

catfish and crayfish, respectively. Detection limits for visceral tissue were 0.017 ppm and 0.007 ppm for catfish and crayfish, respectively.

REPORTED RESULTS:

[^{14}C]Glyphosate residues in the water ranged from ~0.88 ppm to ~0.025 ppm during aging (Table 1). During the exposure portion of the study, [^{14}C]glyphosate residue concentrations in the water increased from ~0.04 ppm at day 0 to ~0.09 ppm on day 3 followed by a gradual decrease to 0.064 ppm at day 28. Centrifuging the samples had little effect on the [^{14}C] glyphosate residues in the water. [^{14}C]Glyphosate residues detected in the soil were variable throughout the study (Table 1).

[^{14}C]Glyphosate residues in the catfish accumulated with maximum bioconcentration factors of 2.90x (day 28) and 13.75x (day 21) in the edible and visceral tissue, respectively (Table 2). In crayfish, [^{14}C]glyphosate residues accumulated with maximum bioconcentration factors of 5.8x (day 28) and 72x (day 21) in the edible and visceral tissue, respectively. The concentration of [^{14}C]glyphosate residue in catfish tissue declined from ~0.19 ppm (edible) and ~0.77 ppm (visceral) to ~0.10 ppm (edible) and ~0.12 ppm (visceral) after depuration for 28 days. Concentrations of [^{14}C]glyphosate residues in crayfish edible and visceral tissue were variable during the depuration phase of the study (Table 2).

DISCUSSION:

1. A static, rather than a flow-through exposure system was used.

2. [^{14}C]Glyphosate residues in water, soil, catfish and crayfish tissues were not characterized.

3. Data presented for [^{14}C]glyphosate residues detected in crayfish tissue were too variable to provide useful information on the accumulation of glyphosate in crayfish.

4. The test organisms were not sampled and analyzed on day 0 of the exposure period.

5. [^{14}C]Glyphosate residue concentrations were approximately the same in centrifuged and uncentrifuged water; consequently, all bioconcentration factors were calculated using the uncentrifuged values.

6. The test substance should not be aged.

Table 1. [^{14}C]Glyphosate residues (ppm)[a] detected in soil and water after soil treatment with [^{14}C]glyphosate at 14.3 ppm.

Sampling interval (days)[b]	Soil	Water	
		Centrifuged	Uncentrifuged
Aging			
0	32.0 ± 11	--	--
3	24.0 ± 10	--	--
4	4.0 ± 2.8	0.88 ± 0.75	--
15	9.3 ± 3.5	0.59 ± 0.089	0.53 ± 0.014
30	9.8 ± 5.8	0.025 ± 0.00	0.025 ± 0.001
Exposure			
0	4.5 ± 1.7	0.043 ± 0.001	0.035 ± 0.000
1	7.0 ± 3.2	0.071 ± 0.001	0.067 ± 0.002
3	15.0 ± 3.5	0.089 ± 0.004	0.083 ± 0.001
7	12.0 ± 6.0	0.082 ± 0.003	0.081 ± 0.001
10	8.8 ± 0.8	0.080 ± 0.001	0.079 ± 0.003
14	12.0 ± 0.7	0.084 ± 0.000	0.082 ± 0.000
21	7.8 ± 2.2	0.072 ± 0.001	0.064 ± 0.004
28	7.4 ± 1.2	0.064 ± 0.001	0.062 ± 0.001

[a] Values are mean residues ± standard deviation based on radiometric analyses of three samples per sampling interval.

Table 2. [^{14}C]Glyphosate residues (ppm) detected in edible and visceral tissue of catfish and crayfish after exposure to glyphosate at 14.3 ppm.

Sampling interval (days)[b]	Catfish[a]		Crayfish[b]	
	Edible	Viscera	Edible	Viscera
		Exposure		
1	0.03 ± 0.00	0.10 ± 0.01	0.10 ± 0.08	1.00 ± 1.06
3	0.07 ± 0.01	0.41 ± 0.18	0.18 ± 0.08	1.14 ± 0.88
7	0.11 ± 0.03	0.42 ± 0.06	0.26 ± 0.08	3.20 ± 0.93
10	0.09 ± 0.02	0.55 ± 0.12	0.43 ± 0.18	3.82 ± 2.11
14	0.12 ± 0.02	0.73 ± 0.23	0.28 ± 0.12	3.21 ± 2.14
21	0.12 ± 0.04	0.88 ± 0.14	0.32 ± 0.11	4.62 ± 0.73
28	0.18 ± 0.04	0.74 ± 0.15	0.36 ± 0.19	2.97 ± 0.91
		Depuration		
1	0.19 ± 0.02	0.77 ± 0.11	0.44 ± 0.10	5.00 ± 0.38
3	0.14 ± 0.02	0.59 ± 0.15	0.58 ± 0.30	2.52 ± 1.87
7	0.16 ± 0.04	0.51 ± 0.07	0.65 ± 0.58	3.28 ± 2.85
10	0.13 ± 0.04	0.37 ± 0.12	--	--
14	0.12 ± 0.04	0.26 ± 0.08	0.34 ± 0.21	1.91 ± 1.38
21	0.11 ± 0.02	0.33 ± 0.06	--	--
28	0.10 ± 0.04	0.12 ± 0.04	--	--

[a] Values are mean residues ± standard deviation based on 10 and 5 radiometric analyses of catfish muscle and visceral tissue, respectively.

[b] Values are mean residues ± standard deviation based on 10 and 16 radiometric analyses of crayfish muscle and visceral tissue respectively. Values muscle and visceral tissue collected during the depuration phase are mean ± standard deviation of 6 and 3 radiometric analyses, respectively.

CASE GS0178 GLYPHOSATE STUDY 6 PM 25 06/16/83

CHEM 103601 Isopropylamine glyphosate

BRANCH EFB DISC 30 TOPIC 050530 GUIDELINE 40 CFR 163.62-10b

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00108140 CONTENT CAT 01

Monsanto Co. 1975. Residue and metabolism studies in sugarcane and soils. Compilation; unpublished study received July 1, 1976 under 6G1826; CDL:096972-B.

SUBST. CLASS = S.

DIRECT RVW TIME = 18 (MH) START-DATE END DATE

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CONCLUSIONS:

Field Dissipation - Aquatic and Aquatic Impact Uses

This portion of the study is scientifically invalid because the test duration and the sampling protocol were inadequate to accurately assess the dissipation of glyphosate and the patterns of formation and decline of degradates in water. In addition, this portion of the study would not fulfill EPA Data Requirements for Registering Pesticides because the test substance was not characterized and soil and sediment samples were not taken.

Mobility - Leaching and Adsorption/Desorption

1. This portion of the study is scientifically valid.

2. [^{14}C]Glyphosate (purity unspecified) at concentrations ranging from 0.21 to 50.1 ppm, was highly adsorbed to five soils with organic matter contents ranging from 2.40 to 15.50%. Adsorption of glyphosate ranged from 71% (Soil E, 2.4% organic matter, pH 7.29) to 99% (Soil C, 15.5% organic matter, pH 5.35).

3. This portion of the study would not fulfill EPA Data Requirements for Registering Pesticides because complete soil characteristics were not reported, the study was not run in calcium ion solution, K_d values were not reported, desorption of glyphosate was not assessed, and the test substance was not completely characterized.

Metabolism - Aerobic Soil

This portion of the study is scientifically invalid because the sampling protocol was inadequate to accurately assess the decline of glyphosate and the formation and decline of degradates in soil. In addition, this portion of the study would not fulfill EPA Data Requirements for Registering Pesticides because the study was not run at a constant temperature, complete analytical methods were not reported, complete soil characteristics were not reported, and the test substance was not completely characterized.

Metabolism - Anaerobic Soil

This portion of the study is scientifically invalid because the sampling protocol was inadequate to accurately assess the decline of glyphosate and the formation and decline of degradates in soil. In addition, this portion of the study would not fulfill EPA Data Requirements for Registering Pesticides because the study was not run at a constant temperature, complete analytical methods were not reported, complete soil characteristics were not reported, and the test substance was not completely characterized.

MATERIALS AND METHODS:

Field Dissipation - Aquatic and Aquatic Impact Uses

Three irrigation ditches (100 ft x 10 ft; closed at one end and containing full stands of emerged weeds) were treated with glyphosate (Roundup, test substance uncharacterized, source unspecified) at 10 lb ai/A. After 24 hours, water was run into the ditches to a sufficient depth (5 to 8 inches) to induce runoff into irrigation lines.

Water samples were collected 25, 50, 75, and 100 feet along the ditch and at a point 50 feet along the irrigation lines. The samples were cleaned on ion exchange resin columns and fractionated by column chromatography. The appropriate eluate fractions containing glyphosate and aminomethylphosphonic acid were collected. The samples were evaporated, followed by dissolution in trifluoroacetic acid and methylation with

diazomethane. The methylated samples were analyzed by GLC, equipped with a flame photometric detector. The detection limit for glyphosate and aminomethylphosphonic acid was 0.0025 ppm. Recovery values ranged from 67 to 71% and 47 to 90% for glyphosate and aminomethylphosphonic acid, respectively.

Mobility - Leaching and Adsorption/Desorption

Samples (1.0-g) of five Hawaiian soils (Table 2) were treated with [^{14}C]glyphosate (specific activity 9.07 mCi/mM, purity and source unspecified) solution at 0.21, 0.845, 4.92, 9.96, 25.0, and 50.1 ppm. The soil solutions were shaken for three hours and centrifuged. Aliquots of the supernatant were analyzed for radioactivity using LSC.

Metabolism - Aerobic Soil

Experiment 1

Samples (5.0-g) of two soils (Table 3) were placed in flasks and treated with [^{14}C]glyphosate (specific activity 9.07 mCi/mM, purity and source unspecified) at ~10 ppm. Radioactivity evolved as $^{14}CO_2$ was trapped in ascarite by flushing the system with CO_2-free air and quantified on a periodic basis (intervals and analytical methods not reported).

After 35 days of incubation, soil samples were extracted with water and 0.5 N ammonium hydroxide and the extracts were analyzed for total radioactivity by LSC. In addition, aliquots of the extracts were concentrated and spotted on TLC plates. The plates were developed either one dimensionally (using a solution of 1.2 g disodium EDTA: 100 ml 17 N ammonium hydroxide:475 ml water:350 ml 1-propanol:75 ml 1-butanol:2.5 l isobutyric acid) or two dimensionally (using a solution of 37.2 mg disodium EDTA:84 ml 90% aqueous phenol:1-ml glacial acetic acid:16 ml water; followed by the solvent described above) and autoradiographed. Radioactivity remaining in the extracted soil was quantified by combustion analysis.

Experiment 2

Samples (5.0-g) of five soils (Table 4) were placed in flasks and adjusted to ~0.33 bar moisture. Each flasks was treated with [^{14}C]glyphosate (specific activity 1.87 mCi/mM, purity and source unspecified) at ~406 ppm. Radioactivity evolved as $^{14}CO_2$ was captured in ethanolamine:ethylene glycol monomethyl ether (1:2, v:v) trapping solution and quantified by LSC.

The soil samples were analyzed by extraction and LSC, total combustion, and TLC as described in Experiment 1.

Metabolism - Anaerobic Soil

Flasks from Experiment 1 (Metabolism - Aerobic Soil) were flushed with nitrogen gas to establish anaerobic conditions. Radioactivity evolved as $^{14}CO_2$ and in soil samples, taken at 35 days posttreatment, was analyzed as described in Experiment 1 (Metabolism - Aerobic Soil).

REPORTED RESULTS:

Field Dissipation - Aquatic and Aquatic Impact Uses

Irrigation ditch water, introduced and sampled one day after dry ditch glyphosate treatment at 10 lb ai/A contained a mean concentration of 0.58 ppm (Table 1). Glyphosate was detected in water samples taken from the irrigation lines at 0.0045 ppm (ditch #1) and 0.58 ppm (ditch #3). Aminomethylphosphonic acid was detected at concentrations up to 0.025 ppm in ditch water and at 0.083 ppm in one irrigation line water sample.

Mobility - Leaching and Adsorption/Desorption

[^{14}C]Glyphosate was highly adsorbed to all soils at all concentrations applied (Table 2). Soil E, with the lowest pH and organic matter content had the widest adsorption range of all soils (from 71% adsorbed at 50.1 ppm applied to 92% adsorbed at 0.21 ppm applied).

Metabolism - Aerobic Soil

Experiment 1

Radioactivity evolved as $^{14}CO_2$ and the radioactivity bound in the extractable and unextractable forms for the two soils are shown in Table 3. Of the radioactivity detected in the soil extracts, 100% was in the form of parent glyphosate for soil G, while in the soil F extracts, 13.3% of the extracted radioactivity was parent glyphosate and 86.7% was aminomethylphosphonic acid.

Experiment 2

Radioactivity evolved as $^{14}CO_2$ and the radioactivity bound in the extractable and unextractable forms for the five soils are shown in Table 4.

Metabolism - Anaerobic Soil

Radioactivity evolved as $^{14}CO_2$ and the radioactivity bound in the extractable and unextractable forms are shown in Table 5. All the radioactivity in soil G was identified as parent glyphosate; in soil F, 13.6% and 86.4% was identified as parent and aminomethylphosphonic acid, respectively.

DISCUSSON:

All Studies

The test substance was not completely characterized.

Field Dissipation - Aquatic and Aquatic Impact Uses

1. The test duration (one day) and the sampling protocol (one sampling interval) were inadequate to accurately assess the dissipation of glyphosate and the patterns of formation and decline of degradates in water.

2. The variation of glyphosate detected in three ditches treated at the same application rate (average concentration for ditch 1 was ~0.03 ppm, while the average concentration for ditches 3 and 4 was ~0.61 ppm and 0.85 ppm, respectively) was not explained.

3. The soil and sediments were not sampled.

Mobility - Leaching and Adsorption/Desorption

1. Complete soil characteristics, such as textural analysis and CEC, were not reported. Consequently, a textural class could not be assigned to individual soils.

2. Values of soil/water (K_d) relationships were not reported.

3. The study was not run in calcium ion solution.

4. Detection limits and recovery values were not reported.

5. Desorption of glyphosate was not addressed.

Metabolism - Aerobic and Anaerobic Soil

1. Complete soil characteristics, such as CEC and textural analysis, were not reported. Consequently, a textural class could not be assigned to the individual soils.

2. The sampling protocol (one sampling interval) was inadequate to accurately assess the decline of glyphosate and the formation and decline of degradates in soil.

4. It was not reported whether the flasks were maintained at a constant temperature.

5. Detection limits and recovery values were not reported.

Table 1. Glyphosate and aminomethylphosphonic acid (ppm) detected in irrigation water from ditches treated at 10 lb ai/A.

	Sampling site				
	25	50	50[a]	75	100
			Ditch #1		
Glyphosate	0.0028	0.033	0.045	0.051	--[b]
AMPA[c]	ND[d]	ND	ND	0.0042	--
			Ditch #2		
Glyphosate	0.07	0.18	--	0.52[e]	1.02[e]
AMPA	ND	ND	--	0.0049[e]	0.0093[e]
			Ditch #3		
Glyphosate	0.57	0.64[f]	0.58	0.89	1.52
AMPA	0.0089	0.0085[f]	0.0083	0.012	0.025

[a] Samples were taken from the 50-foot point of the irrigation lines.

[b] Not sampled.

[c] Aminomethylphosphonic acid.

[d] Not detected; detection limit was 0.0025 ppm.

[e] Values represent the average of three samples.

[f] Values represent the average of two samples.

Table 2. [^{14}C]Glyphosate adsorbed (% of applied) to five soils[a] treated at various concentrations and shaken for three hours.

	Concentration (ppm)					
	0.21	0.84	4.92	9.96	25.0	50.1
Soil A	98	98	98	98	98	98
Soil B	99	98	98	98	98	98
Soil C	99	98	98	98	98	98
Soil D	96	94	93	92	92	93
Soil E	92	86	80	78	72	71

[a] Soil A had 5.75% organic matter with a 5.5 pH; Soil B had 10.25% organic matter with a 5.49 pH; Soil C had 15.50% organic matter with a 5.35 pH; Soil D had 2.85% organic matter with a 7.0 pH; Soil E had 2.4% organic matter with a 7.29 pH; no other soil characteristics were reported.

Table 3. Radioactivity detected (% of applied) in two soils[a] treated with [^{14}C]glyphosate at 10.0 ppm and aerobically incubated for 35 days.

	Extractable				
	Water	Ammonium hydroxide	Nonextractable	$^{14}CO_2$	Total recovered
Soil F	~0.07	79.9	28.2	1.01	109.2
Soil G	1.37	18.2	5.7	60.9	86.2

[a] Soil F contained 7.0% organic matter and had a pH of 7.2; Soil G had 14.0% organic matter with a pH of 5.0; no other soil characteristics were reported.

Table 4. Radioactivity detected (% of applied) in five soils[a] treated with [^{14}C]glyphosate at ~406 ppm and aerobically incubated for 60 days.

	Extractable				
	Water	Ammonium hydroxide	Nonextractable	$^{14}CO_2$	Total recovered
Soil H	4.2	19.2	5.7	65.6	94.7
Soil I	1.8	10.1	8.2	57.7	77.8
Soil J	1.5	40.8	20	35.3	98.2
Soil K	0.02	50.7	33.2	1.2	85.1
Soil L	0.03	66.8	32.1	0.8	99.7

[a] Soil H had 4.6% organic matter with a 6.9 pH; Soil I had 8.9% organic matter with a 7.0 pH; Soil J had 14.15% organic matter with a 6.1 pH; Soil K had 14.25% organic matter with a 5.7 pH; Soil L had 17.50% organic matter with a 5.5 pH; no other soil characteristics were reported.

Table 5. Radioactivity detected (% of applied) in two soils[a] treated with [^{14}C]glyphosate at 10.0 ppm and anaerobically incubated for 35 days.

	Extractable				
	Water	Ammonium hydroxide	Nonextractable	$^{14}CO_2$	Total recovered
Soil F	~0.03	82.9	23.0	1.75	107.7
Soil G	1.67	22.3	7.3	30.9	62.2

[a] Soil F contained 7.0% organic matter with a pH of 7.2; Soil G had 14.0% organic matter with a pH of 5.0; no other soil characteristics were reported.

CASE GS0178 GLYPHOSATE STUDY 13 PM 25 06/16/83

CHEM 103601 Isopropylamine glyphosate

BRANCH EFB DISC 30 TOPIC 050525 GUIDELINE 40 CFR 163.62-9b/c/d

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00037690 CONTENT CAT 01

Monsanto Company. 19??. Soil dissipation of Roundup, Lasso and cyanazine herbicides. Unpublished study received Apr. 18, 1979 under 524-285; CDL:238167-E.

SUBST. CLASS = S.

DIRECT RVW TIME = 5 1/2 (MH) START-DATE END DATE

REVIEWED BY: W. Frantz
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CONCLUSION:

Dissipation - Combination Products and Tank Mix Uses

This study could not be validated because the analytical methods were not described. Currently, data requirements for combination products and tank mix uses are not being imposed for this Standard.

CASE GS0178 GLYPHOSATE STUDY 7 PM 25 06/16/83

CHEM 103601 Isopropylamine glyphosate

BRANCH EFB DISC 30 TOPIC 101020

FORMULATION 15 - SOLUBLE CONCENTRATE

FICHE/MASTER ID 00077238 CONTENT CAT 01

Dubelman, S., and J.R. Steinmetz. 1981. Glyphosate residues in water following application of Roundup herbicide to flowing bodies of water: MSL-1486. Final rept. Includes method dated Sep. 4, 1980. Unpublished study received July 1, 1981 under 524-308; prepared in cooperation with Analytical Biochemistry Labs, submitted by Monsanto Co., Washington D.C.; CDL:070170-R.

SUBST. CLASS = S.

DIRECT RVW TIME = 11 (MH) START-DATE END DATE

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CONCLUSION:

Field Dissipation - Aquatic and Aquatic Impact Uses

This study is scientifically invalid because the sampling protocol was inadequate to accurately assess the dissipation of glyphosate and the pattern of formation and decline of degradates in water. In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides because the test substance was not characterized, complete field test data were not reported, sediments were not sampled or characterized, and the patterns of formation and decline of degradates other than aminomethylphosphonic acid were not addressed.

MATERIALS AND METHODS:

Glyphosate (Roundup, test substance uncharacterized, source unspecified), at 3 lb ai/A, was applied to 100 feet of flowing water at thirteen sites in ten states (Table 1). Water samples were taken from 50 feet downstream of the treated area at pretreatment and at 25, 50, and 75% of the time required for the treated water to pass the sampling point (based on flow-rate calculations), and stored frozen for later analysis.

Water samples were eluted through resin columns with distilled water followed by 0.2 M ammonium carbonate to remove the adsorbed glyphosate and aminomethylphosphonic acid and 0.5 M ammonium carbonate (to remove the adsorbed N-nitrosoglyphosate). The fractions collected were each evaporated and the residues were dissolved in deionized water. The dissolved residues were eluted through resin columns and the glyphosate, aminomethylphosphonic acid, and N-nitrosoglyphosate containing fractions collected for quantitation. The samples were made basic with ammonium hydroxide or ammonium carbonate, evaporated and brought back into solution with deionized water (N-nitrosoglyphosate fraction) or trifluoroacetic anhydride (glyphosate and aminomethylphosphonic acid fraction). Samples containing the N-nitrosoglyphosate degradate were quantified using LSC while those containing glyphosate and aminomethylphosphonic acid were quantified using GLC with a flame photometric detector. Detection limits were 5 ppb for glyphosate and aminomethylphosphonic acid and 2 ppb for N-nitrosoglyphosate.

Recovery values averaged 61.6, 59.6, and 70.5% for glyphosate, aminomethylphosphonic acid, and N-nitrosoglyphosate, respectively.

REPORTED RESULTS:

Glyphosate in flowing water samples collected 50 feet downstream from the treated areas ranged from undetectable to ~1900 ppb while aminomethylphosphonic acid ranged from undetectable to ~14 ppb (Table 2). N-nitrosoglyphosate was not detected in any of the water samples.

DISCUSSION:

1. Complete field test data, including water treatment dates, temperature, pH, dissolved oxygen content, and percent suspended solids, were not reported for all sites. Meteorological data and sediment characteristics were not provided.

2. The sampling protocol was inadequate to accurately assess the dissipation of glyphosate and patterns of formation and decline of degradates in water. The sampling times were calculated based on the individual flow rate of the various streams and ranged from ~1.8 to ~8.0 minutes after treatment. Sediment samples were not collected for analysis.

(% of applied) in five soils[a] treated
~406 ppm and aerobically incubated

ım ide	Nonextractable	$^{14}CO_2$	Total recovered
	5.7	65.6	94.7
	8.2	57.7	77.8
	20	35.3	98.2
	33.2	1.2	85.1
	32.1	0.8	99.7

ı a 6.9 pH; Soil I had 8.9% organic
l.15% organic matter with a 6.1 pH;
th a 5.7 pH; Soil L had 17.50% or-
r soil characteristics were reported.

STUDY 6

two soils[a] treated
ɛrobically incubated

ıctable	$^{14}CO_2$	Total recovered
0	1.75	107.7
3	30.9	62.2

of 7.2; Soil G had 14.0%
characteristics were reported.

3. The test substance was not characterized.

4. Water samples were taken from approximately halfway between the surface and the bottom of the streams.

Table 1. Site characteristics.

Location	Site types	Water temperature (F)	Stream depth (ft)	Water flow rate (ft/sec)	Air temperature (F)
Richmond, Utah #1	Stream	50	1.5	1.92	--
Richmond, Utah #2	Stream	50	1.5	1.92	--
Boliver, Tennessee	Stream	--	1.3	1.69	--
Fairfield, Montana	--[a]	68	1.0	2.00	88
Walker, Louisiana	Stream	76	1.0	1.43	80
Upperco, Maryland	Stream	--	1.15	0.48	--
Stevenson, Alabama	--	94	0.83	0.0694	--
El Paso, Texas #1	Concrete irrigation ditch	--	~1.3	1.11	--
El Paso, Texas #2	Concrete irrigation ditch	--	~1.3	1.11	--
Stockridge, Michigan	Stream	76	0.8-1.0	0.7	80
Ft. Pierce, Florida #1	Stream	84	--	0.55	90
Ft. Pierce, Florida #2	Stream	84	2.5-3.0	0.55	90
Syracuse, New York	Stream	--	.75	0.625	--

[a] Not reported.

Table 2. Glyphosate and aminomethylphosphonic acid (ppb) detected in water samples taken from flowing water treated with glyphosate at 3.75 lb ai/A.

Location	Sample 1[a]		Sample 2		Sample 3		Sample 4	
	Glyphosate	AMPA[b]	Glyphosate	AMPA	Glyphosate	AMPA	Glyphosate	AMPA
Richmond, Utah #1	ND[c]	ND	ND	ND	ND	ND	ND	ND
Richmond, Utah #2	ND	ND	ND	ND	ND	ND	11.34	ND
Boliver, Tennessee	ND	ND	334.89	ND	388.65	ND	104.02	ND
Fairfield, Montana	ND	ND	32.72	ND	49.28	ND	95.62	ND
Walker, Louisiana	<5.38	ND	1582.69	13.68	1915.60	14.15	1549.39	13.31
Upperco, Maryland	ND	ND	ND	ND	<5.43	ND	ND	ND
Stevenson, Alabama	7.59	ND	221.95	ND	305.78	ND	110.06	ND
El Paso, Texas #1	ND	ND	331.55	ND	230.05	ND	281.34	ND
El Paso, Texas #2	ND	ND	242.96	ND	250.96	ND	183.43	ND
Stockridge, Michigan	<5.04	ND	341.61	8.32	657.62	6.29	442.87	6.98
Ft. Pierce, Florida #1	63.38	ND	422.55	7.13	197.35	ND	243.14	ND
Ft. Pierce, Florida #2	12.66	ND	628.73	ND	506.19	ND	839.99	ND
Syracuse, New York	ND	ND	11.37	ND	54.04	ND	65.31	ND

[a] Sampling times were calculated based on the individual flow rate from each site. Samples were taken at pre-treatment (sample 1) and at 25, 50, and 75% of the time required for the treated water to pass to sampling site (2, 3, and 4, respectively).

[b] Aminomethylphosphonic acid.

[c] Not detected; the detection limit was 5 ppb.

CASE GS0178 GLYPHOSATE STUDY 8 PM 25 06/16/83

CHEM 103601 Isopropylamine Glyphosate

BRANCH EFB DISC 30 TOPIC 05

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00108192 CONTENT CAT 01

Brightwell, B., and J. Malik. 1978. Solubility, volatility, adsorption and partition coefficients, leaching, and aquatic metabolism of MON 0573 and MON 0101: Report No. MSL-0207. Final rept. Unpublished study received June 12, 1978 under 524-308; submitted by Monsanto Co., Washington, DC; CDL:234108-A.

SUBST. CLASS = S.

DIRECT RVW TIME = 27 (MH) START-DATE END DATE

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CONCLUSIONS:

Degradation - Hydrolysis

1. This portion of the study is scientifically valid.

2. [^{14}C]Glyphosate (94% glyphosate, 5.9% aminomethylphosphonic acid) and aminomethylphosphonic acid were stable in sterile buffered water at pH 3, 6, and 9 during 35 days of incubation in the dark at 5 and 35 C. Slight degradation of [^{14}C]glyphosate was observed in two of three sterile, natural waters treated with [^{14}C]glyphosate (94% glyphosate, 5.9% aminomethylphosphonic acid), at 0.1 ppm, and incubated in the dark at 30 C for 35 or 49 days. Aminomethylphosphonic acid was detected at maximum concentrations of 25.3 and 17.2 % of the applied 35 days posttreatment in the Cattail Swamp (pH 6.2) and Ballard Pond (pH 7.3) waters, respectively. No degradation was observed in Sphagnum Bog water (pH 4.2).

3. This portion of the study fulfills EPA Data Requirements for Registering Pesticides by providing information on the hydrolysis of glyphosate and the glyphosate degradate aminomethylphosphonic acid in sterile, buffered water at pH 3, 6, and 9 at 5 and 35 C.

Metabolism - Aerobic Aquatic

1. This portion of the study is scientifically valid.

2. [^{14}C]Glyphosate (94% glyphosate, 5.9% aminomethylphosphonic acid) degraded in three natural waters at pH 4.2, 6.2, and 7.3, with 39-49% of the applied remaining at 49 days, 51-61% at 63 days, and 58-69% at 35 days, respectively. Respective aminomethylphosphonic acid concentrations increased steadily at each sampling interval, reaching maximum concentrations in the Sphagnum Bog, Cattail Swamp, and Ballard Pond waters of 26.2, 30.2, and 23.1% of the applied radioactivity. A maximum of 29, 14.6, and 11.4% of the applied radioactivity evolved as $^{14}CO_2$ in the pH 4.2 (day 63), pH 6.2 (day 63), and pH 7.3 (day 35) waters, respectively. Addition of sediment to the system increased the dissipation of glyphosate and aminomethylphosphonic acid from water via adsorption to sediment. Evolution of $^{14}CO_2$ was not affected. All samples were maintained at 30 C in the dark.

3. This portion of the study does not fulfill EPA Data Requirements for Registering Pesticides because the test waters were not mixed with sediment or soil (Experiment 1), complete water characteristics were not provided, and data on the characterization of radioactivity were not provided for all sampling intervals.

Mobility - Adsorption/Desorption

1. This portion of the study is scientifically valid.

2. [^{14}C]Glyphosate (94% glyphosate, 5.9% aminomethylphosphonic acid) was adsorbed to Drummer silty clay loam, Ray silt, Spinks sandy loam, Lintonia sandy loam, and Cattail Swamp sediment with Freundlich K values of 62, 90, 70, 22, and 175, respectively. The maximum percentages of applied glyphosate desorbed were 5.3, 3.7, 3.6, 11.5, and 0.9%, respectively.
3. This study partially fulfills EPA Data Requirements for Registering Pesticides by providing information on the adsorption/desorption of glyphosate in silty clay loam, silt, and two sandy loam soils. Data pertaining to the Cattail Swamp sediment do not contribute to data requirements because the characteristics were incompletely provided.

Mobility - Column Leaching

1. This portion of the study is scientifically valid.

2. [^{14}C]Glyphosate (94% glyphosate, 5.9% aminomethylphosphonic acid) was slightly mobile to relatively immobile with <7% of the applied ^{14}C detected in the leachate from 30-cm silt, sand, clay, sandy clay loam, silty clay loam, and sandy loam soil columns eluted with 20 inches of water. Aged (30 days) [^{14}C]glyphosate residues were relatively immobile in silt, clay, sandy clay loam soils with <2% of the radioactivity detected in the leachate following elution with 20 inches of water. Both glyphosate and amino-

methylphosphonic acid were detected in the leachate of aged and unaged soil columns.

3. This study partially fulfills EPA Data Requirements for Registering Pesticides by providing information on the mobility of glyphosate (unaged) in sand, silt, clay, sandy clay loam, silty clay loam, and two sandy loam soils and on the mobility of glyphosate residues (aged) in silt, clay, and sandy clay loam soils.

MATERIALS AND METHODS:

Degradation - Hydrolysis

Three buffered (pH 3, 6, and 9) waters containing 0.05% formalin as a mold inhibitor, were treated with filtered (Millipore 0.45 µm) [^{14}C]glyphosate (94% glyphosate, 5.9% aminomethylphosphonic acid; Monsanto Co.), at 25 and 250 ppm. Aliquots (1 ml) were transferred to vials, and incubated in the dark at 5 and 35 C. Samples were taken at 0, 7, 14, 21, and 35 days posttreatment.

Additionally, water from three field sites, Cattail Swamp, Sphagnum Bog, and Ballard Pond (pH 6.2, 4.2, and 7.3, respectively), was collected, treated with [^{14}C]glyphosate (94% glyphosate, 5.9% aminomethylphosphonic acid; Monsanto Co.), at 0.1 ppm, sterilized (Millipore filter 0.45 µm), and incubated in the dark at 30 C. Aliquots (20 ml) were taken immediately after treatment and at 7, 21, 35, and 49 days (Cattail Swamp only) posttreatment.

All samples, in duplicate, were analyzed for radioactivity by LSC. Samples were analyzed for glyphosate and aminomethylphosphonic acid by TLC and HPLC. The material balance was >90% for all samples. Detection limits were not reported.

Metabolism - Aerobic Aquatic

Experiment 1

Three natural waters (see hydrolysis study), in 250 ml flasks fitted with Ascarite traps, were treated with [^{14}C]glyphosate (94% glyphosate, 5.9% aminomethylphosphonic acid; Monsanto Co.), at 0.1 ppm. The flasks were incubated at 30 C in the dark for 9 weeks. Aliquots (size not specified) were taken at 0, 1, 3, 5, 7, and 9 weeks posttreatment. The $^{14}CO_2$ evolved was trapped and quantified directly by LSC. Water samples were analyzed for glyphosate and the glyphosate degradate aminomethylphosphonic acid, by HPLC and TLC. Total radioactivity recovered ranged from 92 to 108%. Detection limits were not reported.

Experiment 2

Sediments and waters (100 ml:100 ml) from two Wisconsin sites, the Cattail Swamp and Sphagnum Bog (see Table 1 and hydrolysis study for characteristics) were added to Erlenmeyer flasks fitted with Ascarite towers to trap the $^{14}CO_2$. Each flask was treated with [^{14}C]glyphosate (94% glyphosate, 5.9% aminomethylphosphonic acid; Monsanto Co.), at 0.1 ppm, and incubated in the dark at 30 C for 7 weeks. Soil and water samples were taken at 3, 7, 21, 35, and 49 days posttreatment. The $^{14}CO_2$ evolved was trapped, and quantified directly by LSC. The contents of the flasks were separated by centrifugation. The sediment fraction was extracted (3x) with 0.5 N NaOH. Water samples and sediment extracts were analyzed for ^{14}C by LSC, and glyphosate and degradate were determined by column chromatography. Water samples and sediment extracts from the last sampling interval (49 days) were also analyzed by HPLC. To determine the radioactivity in sediment not extracted with NaOH, the sediment was lyophilized, combusted, and the $^{14}CO_2$ evolved directly quantified by LSC. Detection limits were not reported. Total radioactivity recovered ranged from 83 to 102 and 88 to 113% of the applied radioactivity in the Sphagnum Bog and Cattail Swamp, respectively.

Mobility - Adsorption/Desorption

Silty clay loam, silt, two sandy loam soils, and a swamp sediment (Table 1) were air-dried and sieved (0.5 mm). Duplicate 2.5-g portions of each soil were mixed with 0.01 N $CaSO_4$ solutions (10 ml) containing [^{14}C]glyphosate (94% glyphosate, 5.9% aminomethylphosphonic acid; Monsanto Co.), at 0, 0.1, 1.0, 10, and 20 ppm. The samples were shaken on a vortex mixer and then mixed mechanically for 4 hours at 25 C. Samples were then centrifuged, and the radioactivity in the supernatant was quantified using LSC.

To measure [^{14}C]glyphosate desorption, the supernatant volume was replaced with an equal volume of 0.01 N $CaSO_4$ solution, shaken for 4 hours with the soil/sediment samples, and again centrifuged. The radioactivity in the supernatant was quantified using LSC. All data were fitted to the Freundlich isotherms. Freundlich K and 1/n values were estimated from log-log plots of the amount of [^{14}C]glyphosate adsorbed versus the equilibrium concentration of [^{14}C]glyphosate in the solution. In the Freundlich equation ($x/m = KC^{1/n}$), x/m is the µg of soil adsorbed/g of soil, C is the equilibrium concentration (µg/ml), and K and 1/n are constants.

Mobility - Column Leaching

Seven soils (Table 1) were air-dried, sieved (2 mm), and added to glass columns (1.5 inches in diameter x 30 cm in height). The soil moisture contents of three soils (Ray silt, Molokai clay, and Hilo sandy clay loam) were adjusted to 15-20% before treatment. All soil column surfaces were treated with [^{14}C]glyphosate (94% glyphosate, 5.9% aminomethylphosphonic acid; Monsanto Co.), at 8 lb ai/A. Following treatment, the Ray silt, Molokai clay, and Hilo sandy clay loam soil columns were fitted with traps to collect evolved $^{14}CO_2$, and incubated (incubation conditions unspecified) for 30 days. The incubated soils were leached

biweekly for 45 days with a total of 20 inches of water added. The other soils were rapidly leached with 20 inches of water.

The leachates from all soil columns were analyzed for radioactivity using LSC. In addition, the leachates from the aged soil columns were combined, concentrated, filtered, and analyzed for glyphosate and aminomethylphosphonic acid by TLC. After the leaching periods, the soil columns were divided into 2-cm segments. Each segment was frozen, lyophilized, combusted, and the $^{14}CO_2$ evolved was trapped and quantified using LSC. An aliquot (2 g) of the top 2-cm segment of the soil columns was extracted twice with 0.5 N NaOH, the combined extracts concentrated, and analyzed by TLC. Recovery values were >78% of the appied for all soil columns. Detection limits were not reported.

REPORTED RESULTS:

Degradation - Hydrolysis

Neither [^{14}C]glyphosate nor aminomethylphosphonic acid hydrolyzed in sterile, buffered waters (Table 2). The hydrolysis of [^{14}C]glyphosate and aminomethylphosphonic acid was not affected by treatment rate, pH, or incubation temperature. Slight degradation of [^{14}C]glyphosate was observed in two of the three sterile, natural waters (Table 3). Aminomethylphosphonic acid was detected at maximum concentrations of 25.3 and 17.2 percent of the applied 35 days posttreatment in the Cattail Swamp and Ballard Pond waters, respectively. No degradation was observed in Sphagnum Bog water.

Metabolism - Aerobic Aquatic

Experiment 1

[^{14}C]Glyphosate degradated from the Sphagnum Bog, Cattail Swamp, and Ballard Pond waters with half-lives of 49, >63, and >35 days, respectively (Table 4). Aminomethylphosphonic acid concentrations steadily increased at each sampling interval, reaching maximum concentrations in the Sphagnum Bog, Cattail Swamp, and Ballard Pond waters of 26.2, 30.2, and 23.1% of the applied.

Experiment 2

The sum of the glyphosate concentrations in the water, and extract of the sediment of the Cattail Swamp (pH 6.2), was similiar to that found in the Sphagnum Swamp (pH 4.2) (Table 5). The partioning of glyphosate between the water and sediment, however, was quite different. In the Cattail Swamp, glyphosate concentrations in water ranged from 5.9 (day 7) to 3.5% (day 49) of the applied. Glyphosate concentrations in sediment for the same sampling period ranged from 52.1 to 58.7% of the applied. At day 49 of the incubation period, $^{14}CO_2$ and unextractable radioactivity accounted for 17.1 and 23.0% of the applied. At the end

of the sampling period (49 days), [^{14}C]glyphosate, in sediment extract and water from the Sphagnum Bog (pH 4.2), was detected at 28.3 and 20.0%, respectively, of the applied. $^{14}CO_2$ and unextractable radioactivity increased during the 7 weeks to maximum concentrations of 21.8 and 22.1% of the applied.

Mobility - Adsorption/Desorption

Freundlich K values ranged from 22 for the Lintonia sandy loam (organic matter content 0.7%, CEC 5.1 meq/100 g) to 175 for the Cattail Swamp sediment (organic matter content 1.5%) (Table 6). The percent of applied glyphosate desorbed ranged from 11.5 to 0.9% for the Lintonia sandy loam and Cattail Swamp sediment, respectively.

Mobility - Column Leaching

After leaching the unaged soil columns with 20 inches of water, the percent of recovered radioactivity remaining in the soil columns ranged from 93.4 to 100% (Table 7). Of the radioactivity remaining in all the soil columns (aged and unaged), >95% of the recovered remained in the top 14 cm of the columns. After leaching the aged soil columns with 20 inches of water over a 45-day period, <2% of the radioactivity was detected in the leachate (Table 8). The distribution of the radioactivity in the leachate and the top 2-cm segment of the soil columns between glyphosate and the degradate aminomethylphosphonic acid is presented in Tables 9 and 10, respectively.

DISCUSSION:

Degradation - Hydrolysis

Detection limits were not reported.

Metabolism - Aerobic Aquatic

1. Soil/sediment was not included in the experimental design (Experiment 1).

2. Complete water characteristics, including percent suspended solids and dissolved oxygen content, were not reported.

3. Data were not collected long enough to permit the degradation of glyphosate and the pattern of formation and decline of the degradate MON 0453 to be determined.

4. Complete sediment characteristics for the Cattail Swamp, including textural analysis, pH, and CEC, were not reported.

Mobility - Adsorption/Desorption

1. The soils and sediments were sieved to 0.5 mm, thus removing the coarse sand fraction.

2. The test soil reported to be Ray silt loam is a silt according to the USDA soil textural classification system. The soil textural classifications for the Drummer, Spinks, and Lintonia soils could not be verified because the textural analyses were <100%.

Mobility - Column Leaching

1. Values of soil/water relationships (K_d) were not reported.

2. The test soil reported to be Ray silt loam is a silt according to the USDA soil textural classification system. The soil textural classifications for the Drummer, Spinks, and Lintonia soils could not be verified because the textural analyses were <100%.

Table 1. Soil and sediment characteristics.

Soil type	Sand	Silt	Clay	Organic matter	pH	CEC (meq/100 g)
	%					
Ray silt[a]	4.6	84.2	10.0	1.2	8.1	10.4
Drummer silty clay loam[a]	2.4	68.8	25.3	3.4	6.2	24.6
Spinks sandy loam[a]	75.1	17.8	4.8	2.4	4.7	11.3
Lintonia sandy loam[a]	86.0	11.0	1.8	0.7	6.5	5.1
Leon sand	94.0	5.0	1.0	1.0	4.8	7.2
Hilo sandy clay loam	54.0	20.0	26.0	9.5	5.7	60.0
Molokai clay	18.0	30.0	52.0	3.0	7.0	20.0
Ballard Pond sediment	18.0	54.0	28.0	0.7	6.0	21.0
Cattail Swamp sediment	--	--	--	1.5	--	--

[a] See Discussion #2 under Mobility - Adsorption/Desorption.

Table 2. Concentrations (% of applied) of glyphosate and aminomethylphosphonic acid in sterile buffered solutions incubated for 35 days in the dark after treated with [^{14}C]glyphosate, at 25 and 250 ppm, as determined by TLC and HPLC.

pH	Incubation temperature (C)	Treatment rate (ppm)	TLC	HPLC	
			Glyphosate	Glyphosate	MON 0435[a]
3	35	25	91.6	94.6	5.4
		250	92.9		
	5	25	91.8	94.2	5.8
		250	92.0		
6	35	25	91.9	93.7	6.3
		250	93.3		
	5	25	92.9	94.1	5.9
		250	92.7		
9	35	25	92.7	94.1	5.9
		250	94.4		
	5	25	93.3	93.7	6.3
		250	93.9		

[a] Aminomethylphosphonic acid.

Table 3. Concentrations (% of the applied) of glyphosate and MON 0435 (aminomethylphophonic acid) in sterile three natural waters treated with [^{14}C]glyphosate, at 0.1 ppm, and determined by HPLC.

Water	pH	Sampling interval (days)	Glyphosate	MON 0435
Cattail Swamp	6.2	21	90.4	9.6
		35	74.7	25.3
		49	80.7	19.3
Sphagnum Bog	4.2	21	94.4	5.6
		35	94.0	6.0
Ballard Pond	7.3	21	83.8	16.2
		35	82.8	17.2

Table 4. Concentrations (% of applied) of glyphosate and aminomethylphosphonic acid (MON 0435) in three natural waters treated with [^{14}C]glyphosate, at 0.1 ppm, and incubated at 30 C in the dark.

Water	Sampling interval (days)	Radioactivity		TLC		HPLC	
		$^{14}CO_2$	H_2O	Glyphosate	MON-0435	Glyphosate	MON-0435
Sphagnum Bog	3	1.5	102.5	--	--	--	--
	7	2.3	96.0	--	--	--	--
	21	6.6	87.2	79.4	7.8	--	--
	35	13.5	86.1	71.3	14.8	--	--
	49	22.1	71.7	49.4	22.3	38.9	32.8
	63	29.0	63.1	36.9	26.2	27.9	35.2
Cattail Swamp	3	2.1	95.6	--	--	--	--
	7	3.2	97.1	83.5	13.6	--	--
	21	6.5	96.7	73.8	16.7	--	--
	35	10.8	91.8	68.8	23.0	--	--
	49	12.8	91.7	65.7	26.2	66.9	24.8
	63	14.6	91.2	61.0	30.2	50.9	40.3
Ballard Pond	7	4.0	93.7	76.5	17.2	81.4	18.6
	21	8.3	100.4	78.1	22.3	70.6	29.4
	35	11.4	92.0	68.9	23.1	58.4	33.6

Table 5. Concentrations (% of applied) of glyphosphate and aminomethylphosphonic acid (MON 0435) in sediment and water treated with [^{14}C]glyphosate, at 0.1 ppm and incubated aerobically at 30 C in the dark.

		Radioactivity (% of applied)						
			H_2O		Sediment			
					Extractable			
Water	Sampling interval (days)	$^{14}CO_2$	Glyphosate	MON 0435	Glyphosate	MON 0435	Unextractable	Total
Sphagnum Bog	3	0.87	--	--	--	--	--	--
	7	2.67	--	--	--	--	6.52	93.8
	21	16.91	32.9	4.9	15.8	6.8	5.92	83.3
	35	19.46	19.0	2.7	33.6	13.3	7.15	93.8
	49	21.84	20.0	2.7	28.3	6.7	22.09	102.4
Cattail Swamp	3	0.62	--	--	--	--	--	--
	7	1.87	5.9	1.0	52.1	10.2	25.0	95.1
	21	4.83	4.8	1.1	44.5	18.8	13.8	87.8
	35	15.28	3.7	0.4	45.0	15.1	18.9	97.8
	49	17.11	3.5	0.2	58.7	10.1	23.0	112.6

Table 6. Freundlich K and 1/n for the adsorption of glyphosate on a swamp sediment and four soils.

Soil type	K	1/n	Percent desorbed[a]
Ray silt	90	0.902	3.7
Spinks sandy loam	70	0.944	3.6
Drummer silty clay loam	62	0.951	5.3
Lintonia sandy loam	22	0.782	11.5
Cattail Swamp sediment	175	1.010	0.9

[a] Maximum glyphosate desorbed from the four different equilibration concentrations.

Table 7. Distribution of radioactivity (% of recovered) in seven soil columns treated with [^{14}C]glyphosate and rapidly eluted with 20 inches of water.

Sampling depth (inches)	Soil type						
	Lintonia	Ray	Spinks	Leon	Drummer	Hilo	Molokai
0-2	33.4	24.5	72.1	21.2	80.0	99.5	98.6
2-4	25.3	24.3	24.6	19.8	14.3	0.2	0.9
4-6	17.3	18.0	1.8	15.5	2.4	0.2	0.1
6-8	10.4	14.5	0.4	15.4	0.8	0.1	0.3
8-10	4.8	6.8	0.2	10.4	0.4	0.0	0.0
10-12	2.3	2.4	0.1	6.7	0.3	0.0	0.0
12-14	0.8	1.4	0.1	4.1	0.2	0.0	--
14-16	0.4	0.7	0.1	2.4	0.1	0.0	--
16-18	0.2	0.3	0.1	1.9	0.3	0.0	--
18-20	0.1	0.1	0.0	0.8	0.1	0.0	--
20-22	0.1	0.1	0.0	0.3	0.1	--	--
22-24	0.1	0.1	0.0	0.3	0.1	--	--
24-26	0.1	0.1	0.2	0.2	0.0	--	--
26-28	0.1	0.1	0.0	0.1	0.1	0.0	--
28-30	0.1	0.1	0.1	0.1	0.0	0.0	--
Total recovered in soil column	95.6	93.4	99.9	99.0	99.1	100.0	99.9
Total recovered in leachate	4.4	6.6	0.1	1.0	0.9	0.0	0.1
Total recovered	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Percent of applied	78.7	90.5	95.5	99.9	89.0	98.7	101.7

Table 8. Distribution of radioactivity (% of recovered) in three soil columns treated with [^{14}C]glyphosate, incubated for 30 days, and eluted with 20 inches of water over a 45-day period.

Sampling depth (inches)	Soil type		
	Ray silt	Molokai clay	Hilo sandy clay loam
0-2	30.30	40.39	97.53
2-4	1.07	0.20	0.03
4-6	0.49	0.05	0.03
6-8	0.27	0.07	0.01
8-10	0.24	0.07	0.01
10-12	0.17	0.04	0.01
12-14	0.10	0.04	0.01
14-16	0.12	0.02	--
16-18	0.09	0.02	--
18-20	0.11	0.02	--
20-22	0.08	0.02	0.01
22-24	0.05	0.02	0.01
24-26	0.06	0.02	--
26-28	0.08	0.01	--
28-30	0.04	0.01	0.01
Total recovered in soil column	33.26	41.00	97.66
Total recovered in leachate	1.56	0.22	0.02
Total evolved as $^{14}CO_2$	65.18	58.78	2.32
Total recovered	100.00	100.00	100.00
Percent of applied	98.40	84.62	98.94

Table 9. Glyphosate and aminomethylphosphonic acid concentration (% of applied) in the leachate of soils treated with [^{14}C]glyphosate at 8 lb ai/A and eluted with 20 inches of water.

Soil	Glyphosate	Aminomethylphosphonic acid
Ray[a]	0.8	0.7
Hilo[a]	--	--
Molokai[a]	--	--
Ray	5.8	0.8
Lintonia	3.9	0.5
Drummer	0.6	0.3
Spinks	--	--
Leon	0.6	0.4
Hilo	--	--
Molokai	--	--

[a] Incubated 30 days before being leached over a 45-day period.

Table 10. Distribution of radioactivity (% of extractable) between Glyphosate and aminomethylphosphonic acid in the top 2-cm segment of soil columns treated with [^{14}C]glyphosate, at 8 lb ai/A, and leached with 20 inches of water.

Soil	Radioactivity (% of applied)	% extracted	Glyphosate (% of extractable)	Aminomethylphosphonic acid (% of extractable)
Ray[a]	30.3	52.4	26	84
Hilo[a]	97.7	8.4	94	6
Molokai[a]	34.1	47.0	22	78
Ray	234.5	72.3	76	24
Lintonia	33.4	78.9	80	20
Drummer	80.0	77.8	86	14
Spinks	72.1	95.7	90	10
Leon	21.2	99.1	93	7
Hilo	99.5	15.1	94	6
Molokai	98.6	50.3	86	14

[a] Incubated 30 days before treatment; leaching period was 45 days.

CASE GS0178 GLYPHOSATE STUDY 9 PM 25 06/16/83

CHEM 103601 Isopropylamine glyphosate

BRANCH EFB DISC 30 TOPIC 052020

FORMULATION 15 - SOLUBLE CONCENTRATE

FICHE/MASTER ID 00093922 CONTENT CAT 01

Danhaus, R.G., C.M. Lottman, and J.R. Steinmetz, et al. 1979. Roundup Forest Ecosystem: Part II: Residues of glyphosate, aminomethylphosphonic acid and N-nitrosoglyphosate in forest foliage and litter and on mylar spray interceptors, following aerial application of Roundup herbicide: MSL-1974. Unpublished study received Jan. 27, 1982, under 524-308; submitted by Monsanto Co., Washington, DC; CDL:246658-A.

FICHE/MASTER ID 00084657 CONTENT CAT 01

Edwards, G.A. 1981. Roundup herbicide forest ecosystem study: Part I: Residues of glyphosate, aminomethylphosphonic acid and N-nitrosoglyphosate in forest soil and water following aerial application of Roundup herbicide: Special Report MSL-1830. Unpublished study received Oct. 6, 1981, under 524-308; submitted by Monsanto Co., Washington, DC; CDL:246006-A.

SUBST. CLASS = S.

DIRECT RVW TIME =21 (MH) START-DATE END DATE

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Two hardcopies were combined for this review because one hardcopy (00084657) contains soil and water data and the other hardcopy (00093922) contains the foliage and leaf litter data from the same forestry study.

CONCLUSIONS:

Field Dissipation - Forestry

1. This study is scientifically valid.

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2. Glyphosate and aminomethylphosphonic acid concentrations, during the 55 days after treatment with glyphosate (test substance uncharacterized) at 3.0 lb ai/A, ranged from <0.05 to 0.77 ppm (exposed soil); <0.05 to 1.28 ppm (covered soil); <0.05 to 0.55 ppm (sediment); <0.002 to 3.22 ppm (drip water); <0.002 to 0.15 ppm (stream water samples);0.17 to 89.00 ppm (foliage); and 0.20 to 11.00 ppm (leaf litter). N-nitrosoglyphosate was not detected in any samples, expect the stream water, where 0.002 ppm were detected in all samples.

3. This study does not fulfill EPA Data Requirements for Registering Pesticides because complete soil characteristics were not presented, complete field test data were not reported, the test substance was not characterized, and the duration of the study was inadequate to assess the decline of glyphosate and patterns of formation and decline of degradates in a forest ecosystem.

MATERIALS AND METHODS:

Glyphosate (Roundup, test substance uncharacterized, source unspecified), at 3 lb ai/A, was aerially applied to a 20 A test plot near Corvallis, Oregon. Mylar sheets were exposed during treatment to verify the application rate. The sprayed area consisted of loam soil (soil not further characterized) covered with maples, alders, salmonberry and ferns and bisected by a stream. Four sampling sites were established within the plot. Foliage samples (5 lbs/sample) were taken from the trees, shrubs and herbaceous species at pretreatment, immediate post-treatment, and 1, 3, 7, 14, 28, and 55 days posttreatment. Litter (2-3 lb/sample) and soil (0- to 3-inch depth, covered with litter during treatment; 0- to 6-inch depth, from areas exposed during treatment) were taken at the same intervals as the foliage samples. Samples of drip water were taken 1 and 62 days after treatment while stream sediments were sampled at day 0, 7, 14, 28, and 55. Stream water samples were taken from the downstream edge of the treated plot at 5 minute intervals for the first 80 minutes; 30 minute intervals for the next 2.5 hours; and at days 7, 14, 28, and 55 posttreatment. All samples were frozen within 8 hours of collection and stored for analysis.

Soil and sediment samples were adjusted to 10-20% moisture and extracted twice with 0.5 M ammonium hydroxide. The extracts were eluted through resin columns and the eluate fractions containing the glyphosate, aminomethylphosphonic acid and N-nitrosoglyphosate were collected. The fractions containing the N-nitrosoglyphosate were made basic (pH 9) with ammonium hydroxide, evaporated to dryness, and the residue dissolved in deionized water. N-nitrosoglyphosate was quantified by Griess-HPLC. The glyphosate and aminomethylphosphonic acid fractions were combined, evaporated to dryness, and the residue was dissolved in deionized water. Parent glyphosate and aminomethylphosphonic acid were quantified by ninhydrin-HPLC. Water samples

were eluted through resin columns and the individual fractions collected (as for the soil extracts). Glyphosate, aminomethylphosphonic acid and N-nitrosoglyphosate were quantified as previously described. Plant material samples were ground and extracted 3 times with chloroform. The extracts were separated by column chromatography (as previously described) and the fractions were quantified by Griess-HPLC (N-nitrosoglyphosate) and ninhydrin-HPLC (glyphosate and aminomethylphosphonic acid. The detection limits for glyphosate and aminomethylphosphonic acid were 0.05 ppm in soil, plant material and leaf litter and 0.002 ppm in water. The detection limit for N-nitrosoglyphosate was 0.02 ppm in soil, plant material, and leaf litter and 0.002 ppm in water. Average recovery values for glyphosate, aminomethylphosphonic acid, and N-nitrosoglyphosate are shown in Table 1.

REPORTED RESULTS:

Glyphosate, aminomethylphosphonic acid and N-nitrosoglyphosate were not detected in exposed or litter covered soil, foliage, leaf litter, stream water, drip water, or stream sediment prior to application at 3 lb ai/A. Concentrations of glyphosate and aminomethylphosphonic acid were variable in soil, foliage, and leaf litter samples as indicated by the standard deviations (Tables 2-5). In stream water, ~0.15 ppm glyphosate was detected in samples taken the first day after treatment. Concentrations detected dropped to 0.002 ppm by day 7. Glyphosate detected in sediment decreased from 0.55 ppm on day 14 to 0.11 ppm on day 55, while concentrations in drip water decreased from 3.22 ppm on day 1 posttreatment to <0.002 on day 62. In sediment, 0.12 and 0.085 ppm of aminomethylphosphonic acid was detected on days 14 and 28, respectively. No aminomethylphosphonic acid was detected in drip water. Concentrations in stream water were <0.003 ppm for all samples. No N-nitrosoglyphosate was detected in any sample except the stream water, where 0.002 ppm were detected in all samples.

DISCUSSION:

1. The test substance was not characterized.

2. Complete soil characteristics such as textural analysis, organic matter content, CEC, and pH were not provided.

3. Complete field test data, including rainfall, depth to water table, slope, air and soil temperatures, and date of application were not reported. In addition, the position of the trees in the forest canopy, the thickness of the canopy, the thickness and composition of the litter layer, the rate of flow of water into and out of the aquatic system, and the degree of exposure of the stream to the glyphosate spray during application, were not stated.

4. The study was conducted for an inadequate length of time to assess the decline of glyphosate and patterns of formation and decline of degradates in a forest ecosystem.

Table 1. Average recovery (%) of glyphosate, aminomethylphosphonic acid (AMPA) and N-nitrosoglyphosate from fortified soil, water and plant material samples.

	Soil		Sediment	Water		Foliage[a]	Leaf litter
	Covered	Exposed		Drip	Stream		
Glyphosate	82.9	86.5	77.5	80.6	85.8	86.81	85.2
AMPA	62.1	73.6	77.5	90.4	84.6	67.77	45.5
N-nitrosoglyphosate	73.1	82.5	60.0	70.0	85.5	70.56	84.7

[a] Values represent the average recovery from plant material samples taken from the overstory (top and lower canopy) and the understory (herbaceous ground cover and shrubs).

Table 2. Glyphosate concentrations (ppm)[a] detected in soil, sediment stream and drip water after aerial treatment at 3 lb ai/A.

Sampling interval (days)	Soil		Sediment	Water	
	Exposed	Covered		Drip	Stream
0	ND[b]	ND	ND	ND	ND
0-1	--[c]	--	--	--	0.15[d]
1	0.77(0.53)	1.22(1.27)	--	3.22	0.10
3	0.63(0.39)	0.98(0.91)	--	--	0.01
7	0.66(0.50)	1.28(1.40)	0.12	--	0.002
14	0.38(0.24)	1.21(1.44)	0.55	--	0.002
28	<0.30(0.19)	0.33(0.24)	0.28	--	0.002
55	<0.38(0.53)	0.33(0.39)	0.11	--	0.002
62	--	--	--	ND	--

[a] Values are the average of four samples; numbers in parentheses represent the standard deviation of the individual sample concentration from the mean.

[b] Not detected; detection limits were 0.05 ppm (soil) and 0.002 ppm (water).

[c] Not reported.

[d] Values represent an average of 32 water samples taken the first day after treatment.

Table 3. Aminomethylphosphonic acid concentrations (ppm)[a] detected in soil, sediment, stream and drip water after aerial treatment at 3 lb ai/A.

Sampling interval (days)	Soil		Sediment	Water	
	Exposed	Covered		Drip	Stream
0	ND[b]	ND	ND	ND	ND
0-1	--[c]	--	--	ND	0.003[d]
1	ND	<0.11(0.07)	--	--	0.002
3	<0.08(0.03)	0.23(0.17)	--	--	0.002
7	<0.10(0.04)	<0.40(0.56)	ND	--	0.002
14	0.12(0.06)	0.83(0.69)	0.12	--	0.002
28	<0.13(0.08)	0.19(0.11)	0.085	--	0.002
55	<0.11(0.089)	0.44(0.33)	ND	--	0.002
62	--	--	--	ND	--

[a] Values represent the average of four samples; numbers in parenthesis represent the standard deviation of the individual sample concentration from the mean.

[b] Not detected; detection limits were 0.05 ppm (soil) and 0.002 ppm (water).

[c] Not reported.

[d] Values represent an average of 32 water samples taken the first day after treatment.

Table 4. Glyphosate concentrations (ppm)[a] detected in foliage and leaf litter after aerial treatment at 3 lb ai/A.

Sampling interval (days)	Foliage			Leaf litter
	Overstory	Shrub	Herbaceous	
0	84.00(56.7)	89.00(69)	20.40(10.6)	5.00(6.3)
1	5.00(3.2)	3.80(1.5)	3.70(2.8)	11.00(9.0)
3	--[b]	9.30(1.2)	1.20(1.2)	2.90(2.0)
7	1.70(2.1)	5.70(6.0)	1.20(0.7)	2.20(1.7)
14	0.80(0.8)	1.10(0.5)	1.00(0.6)	2.00(1.7)
28	0.40(0.4)	0.60(0.3)	1.00(0.7)	3.90(2.5)
55	0.17(0.10)	0.18(0.08)	0.37(0.2)	0.20(0.1)

[a] Values are the average of four samples; numbers in parentheses represent the standard deviation of the individual sample concentration from the mean.

[b] Not reported.

Table 5. Aminomethylphosphonic acid (ppm)[a] detected in foliage and leaf litter after treatment at 3 lb ai/A.

Sampling interval (days)	Foliage			Leaf litter
	Overstory	Shrub	Herbaceous	
0	0.23(0.13)	<0.26(0.16)	ND[b]	<0.16(0.12)
1	0.07(0.02)	ND	ND	0.39(0.41)
3	ND	0.11(0.03)	ND	0.32(0.19)
7	ND	ND	ND	0.22(0.10)
14	ND	ND	ND	<0.15(0.15)
28	ND	ND	ND	<0.29(0.19)
55	ND	ND	ND	ND

[a] Values represent the average of 4 samples; numbers in parentheses represent the standard deviation of the individual sample concentration from the mean.

[b] Not detected; detection limit was 0.05 ppm.

CASE GS0178 GLYPHOSATE STUDY 10 PM 25 06/16/83

CHEM 103601 Isopropylamine glyphosate

BRANCH EFB DISC 30 TOPIC 05105 GUIDELINE 40 CFR 163.62-10c

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00101561 CONTENT CAT 01

Kramer, R., and R. Blackburn. 1974. Glyphosate dissipation--pond test. Unpublished study received May 17, 1982 under 524-308; submitted by Monsanto Co., Washington, DC; CDL:070863-A.

SUBST. CLASS = S.

DIRECT RVW TIME = 14 (MH) START-DATE END DATE

REVIEWED BY: G. Moore
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CONCLUSION:

Field Dissipation - Aquatic and Aquatic Impact Uses

This study is scientifically invalid because the analytical methods were inadequate to accurately assess the decline of glyphosate in an aquatic environment. In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides because the test substance was not completely characterized, complete field test data were not reported, and the patterns of formation and decline of degradates other than aminomethylphosphonic acid were not addressed, the sediment was not characterized, the analytical methodology was not reported, and more than one compound was applied to the pond.

MATERIALS AND METHODS:

Glyphosate (MON 0139, test substance uncharacterized, source unspecified) was tank mixed with Sterox NJ (MON 0011, test substance uncharacterized, source unspecified) and sprayed over the entire surface of a non-flowing pond (0.843 acres, ~6.3 feet deep) near Fort Lauderdale, Florida, at 8 lb ai of glyphosate plus 8 lb of Sterox NJ/acre. Water samples (1 quart) were taken at pretreatment, 1, 2, 5 and 8 hours, and 1, 2, 3, 7, 14, 21, 36, 63, and 127 days posttreatment. Samples were taken from three depths (1, 3, and 6 feet) at each of five sites (including the center and four radial points) in the pond. Sediment samples were taken at pretreatment, 7, 14, 21, 36, 63, and 127 days posttreatment from the center of the pond. Samples were stored frozen until analysis.

The analytical methods were not reported. The detection limit was 0.05 ppm for the sediment samples and 2.5 ppb for the water. Recovery of glyphosate from fortified samples ranged from 64.2 to 109.3% and 40.8 to 42.9% for water and sediment, respectively. Recovery of the glyphosate degradate aminomethylphosphonic acid from fortified samples ranged from 51.9 to 104.9% and 55.0 to 63.4% in water and sediment, respectively.

REPORTED RESULTS:

Glyphosate dissipated in pond water with a half-life of 14-21 days (Table 1). The concentration of glyphosate at the three water sampling depths had become similar within 72 hours of treatment (Figure 1). No glyphosate was detected (detection limit 2.5 ppb) in the pond water 129 days after treatment. Aminomethylphosphonic acid was <7.6 ppb at all sampling intervals.

Glyphosate in pond sediments increased with time from 190 ppb at day 7 to 680 ppb at day 127 (Table 2). No aminomethylphosphonic acid was detected at any sampling interval.

DISCUSSION:

1. The recovery of glyphosate from fortified sediment and water samples was too variable (<45%) to accurately establish the concentration of glyphosate in the samples. An accurate decline curve could, therefore, not be developed from the data.

2. More than one compound was applied to the test plot and may have affected the dissipation of glyphosate from the water and sediment.

3. The analytical methods were not described.

4. Glyphosate and Sterox NJ were not characterized.

5. Complete field test data, including air and water temperatures, water pH, and rainfall, were not reported.

6. The patterns of formation and decline of degradates (other than aminomethylphosphonic acid) were not addressed.

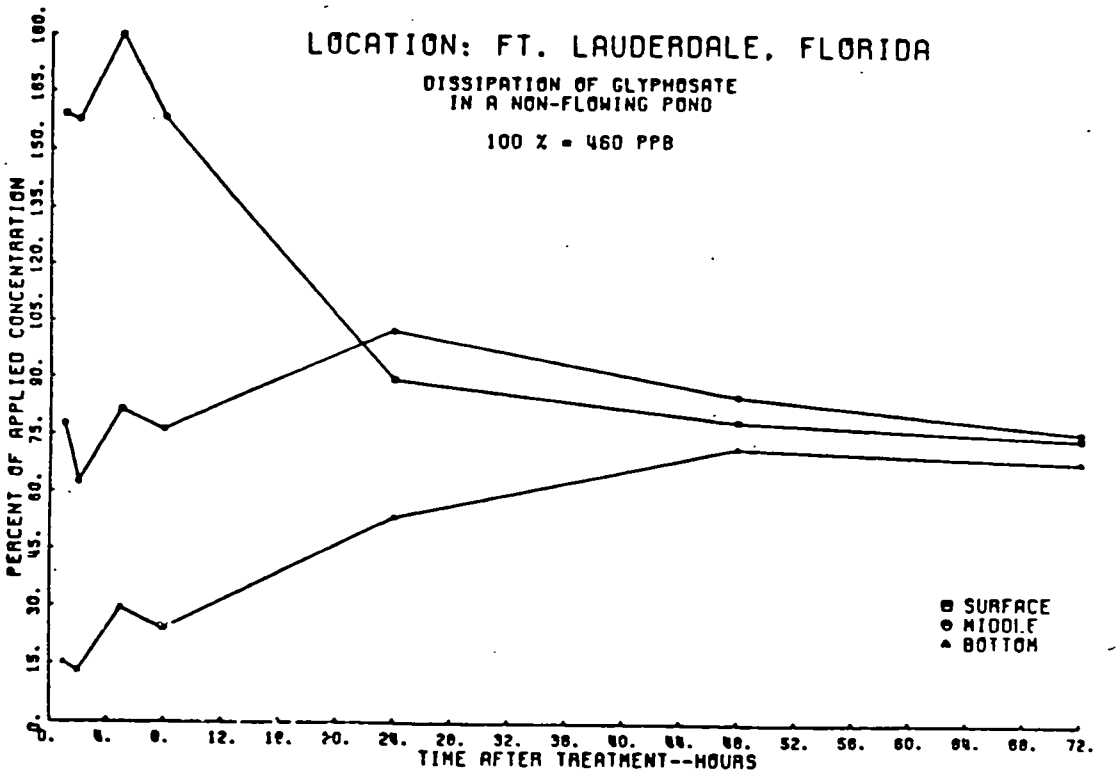

Figure 1. Glyphosate (% of applied) at depths of 1, 3, and 6 feet in a non-flowing pond treated with glyphosate at 8 lb ai/A.

Table 1. Glyphosate (ppb) in water from a non-flowing pond treated with glyphosate at 8 lb ai/A.[a]

Sampling interval	Glyphosate	Aminomethyl-phosphonic acid
Pretreatment	ND[b]	ND
Hours		
1	394	<3.28
2	364	<3.47
5	453	<3.55
8	403	<3.71
Days		
1	379	<3.17
2	362	5.11
3	337	5.12
7	243	7.61
14	255	4.03
21	133	4.01
36	74	4.20
63	22	ND
127	ND	ND

[a] Values represent an average of samples taken at depths of 1, 3, and 6 feet. The initial concentration was calculated to be 460 ppb in 6.3 feet of water which had been treated at 8.0 lb ai/A and well mixed.

[b] Not detected; detection limit was 2.5 ppb.

Table 2. Glyphosate (ppb) in sediment from a non-flowing pond treated with glyphosate at 8.0 lb ai/A.

Sampling interval (days)	Glyphosate[a]	Aminomethyl-phosphonic acid
Pretreatment	ND[a]	ND
7	190	ND
14	260	ND
21	250	ND
36	150	ND
63	440	ND
127	680	ND

[a] Not detected; detection limit was 50 ppb.

CASE GS0178 GLYPHOSATE STUDY 11 PM 25 06/16/83

CHEM 103601 Isopropylamine Glyphosate

BRANCH EFB DISC 30 TOPIC 10142010

FORMULATION 12 - EMULSIFIABLE CONCENTRATE (E or EC)

FICHE/MASTER ID 00108176 CONTENT CAT 01

Monsanto Co. 1975. Residue studies and methods of analysis for pre-emergent use of glyphosate in cotton. Compilation; unpublished study received May 20, 1976 under 6F1978; CDL:098511-A.

FICHE/MASTER ID 00017701 CONTENT CAT 11

Ballantine, L.G., and M.M. Herman. 1979. Bicep plus Roundup or paraquat and Dual/Princep plus Roundup or Paraquat tank mix soil dissipation studies: Report No. ABR-79101. Summary of studies 232193-J, 232193-K, 241545-K, 241545-L and 241545-N. Unpublished study received Jan. 4, 1980 under 100-583; submitted by Ciba-Geigy Corp., Greensboro, NC; CDL:241545-A.

FICHE/MASTER ID 00017706 CONTENT CAT 02

Schnappinger, M.G. 1979. Metolachlor (Dual 8E); simazine (Princep 4L); paraquat (paraquat 2CL); glyphosate (Roundup 4E): AG-A No. 6061 I-VII. Unpublished study including AG-A 5076 and AG-A 5079 XII, received Jan. 4, 1980 under 100-583; prepared in cooperation with En-Cas Analytical Laboratories, Chevron Chemical Co. and A.D.C., submitted by Ciba-Geigy Corp., Greensboro, NC; CDL:241545-N.

SUBST. CLASS = S.

DIRECT RVW TIME = 5 (MH) START-DATE END DATE

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Three hardcopies were combined in this review because one hardcopy (00108176) contained the analytical method, and one hardcopy (00017701) contained the meteorological data, for the dissipation study presented in hardcopy 00017706.

CONCLUSION:

Dissipation - Combination Products and Tank Mix Uses

This study is scientifically invalid because the data were too variable to accurately assess the dissipation of glyphosate alone, or in a combination tank mix with metolachlor and simazine. Currently, data requirements for combination products and tank mix uses are not being imposed for this Standard.

MATERIALS AND METHODS:

Glyphosate (Roundup, 4 lb/gal EC, source unspecified), at 4 lb ai/A, alone and in combination with metolachlor (Dual, 8 lb/gal EC, source unspecified) at 2.5 lb ai/A, and simazine (Princep, 4 lb/gal L, source unspecified) at 2.0 lb ai/A, was applied (broadcast) preemergence to replicate field plots (360 ft^2) located in Maryland on May 22, 1978. The test soil was a sandy loam with 3.6% organic matter (soil not further characterized). Soil samples (0- to 6-inch depth) were taken 0, 30, 58, 125, 182, and 315 days posttreatment from both treated and control plots.

Screened (8 mesh) soil samples (25 g), adjusted to a moisture content between 10-20%, were extracted (4x) with 0.5 M NaOH. Following centrifugation, the combined supernatants were filtered (Whatman #2), and diluted to 1800 ml with distilled water. The diluted sample was added to an ion-exchange chromatography column, and eluted with 0.5 M ammonium bicarbonate. The eluate was shaken with 2 g of charcoal, filtered, and the filtrate evaporated to dryness. The residue was added to a chromatography column, and eluted with deionized water. The first 10 ml fraction eluted was discarded, the next 8 ml fraction, containing parent, retained, and the following 16 ml discarded. The last 20 ml eluted, containing the glyphosate degradate aminomethylphosphonic acid, was retained. The retained eluates were added to separate flasks containing ammonium bicarbonate, evaporated, and then dried completely under nitrogen gas. Each residue was methylated with an excess of methyl pseudourea, and quantified by GC using a flame photometric detector. Recoveries from soil samples fortified with unspecified amounts of glyphosate and aminomethylphosphonic acid, at each sampling interval, ranged from 50 to 78, and 40 to 66%, respectively. The detection limit of both parent and degradate was 0.05 ppm.

REPORTED RESULTS:

The test site received 39.4 inches of rainfall during the test period.

The dissipation of glyphosate, when applied alone or in combination with metolachlor and simazine, from a sandy loam soil located in Maryland, is presented in Table 1. Neither glyphosate nor aminomethylphosphonic acid were detected (<0.05 ppm) in the control plot samples.

DISCUSSION:

1. Complete soil characteristics, such as pH, textural analysis, and CEC, were not provided.

2. Field test data, including depth of water table, slope of test site, rainfall, and soil and air temperature data, were not reported.

3. No pretreatment soil samples were taken.

4. The glyphosate concentrations in the soil immediately after treatment ranged from ~20 to 45% of the reported application rate.

Table 1. Glyphosate and aminomethylphosphonic acid concentrations (ppm)[a] in a sandy loam soil in Maryland, treated with glyphosate alone, or in a combination tank mix of glyphosate (4 lb/gal EC), metolachlor (8 lb/gal EC), and simazine (4 lb/gal L).[b]

Sampling interval (days)	Cumulative rainfall (inches)	Glyphosate	Aminomethylphosphonic acid
		Glyphosate	
0	--	0.40	ND[c]
30	2.6	0.98	ND
58	6.2	0.71	0.05
125	14.7	0.15	ND
182	16.7	0.24	0.06
315	39.4	ND	ND
	Glyphosate in combination with simazine and metolachlor		
0	--	0.89	0.06
30	2.6	0.90	ND
58	6.2	0.47	0.08
125	14.7	0.66	0.06
182	16.7	0.34	ND
315	39.4	0.13	ND

[a] Values were corrected for recoveries and soil moisture contents.

[b] Treatment rates were 2.5, 2.0, and 4.0 lb ai/A for metolachlor, simazine, and glyphosate, respectively.

[c] Not detected; detection limit was 0.05 ppm.

CASE GS0178 GLYPHOSATE STUDY 12 PM 25 06/16/83

CHEM 103601 Isopropylamine glyphosate

BRANCH EFB DISC 30 TOPIC 100520

FORMULATION 12 - EMULSIFIABLE CONCENTRATE (EC OR E)

FICHE/MASTER ID 00017703 CONTENT CAT 02

Schnappinger, M.G. 1978. Metolachlor (Dual 8E) + Atrazine (AAtrex 80 W) + Glyphosate (Roundup 4E): AG-A No. 4597 I-IV. Unpublished study received Jan. 4, 1980 under 100-583; prepared in cooperation with Analytical Development Corp., submitted by Ciba-Geigy Corp., Greenboro, NC; CDL:241545-K.

SUBST. CLASS = S.

DIRECT RVW TIME = 5 (MH) START-DATE END DATE

REVIEWED BY: W. Frantz
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CONCLUSION:

Dissipation - Combination Products and Tank Mix Uses

This study is scientifically invalid because the data were too variable to accurately assess the dissipation of glyphosate from soil when applied alone or in combination with atrazine and metolachlor. Currently, data requirements for combination products and tank mix uses are not being imposed for this Standard.

MATERIALS AND METHODS:

Glyphosate (Roundup, 4 lb/gal EC, source unspecified), at 4 lb ai/A, in combination with metolachlor (Dual, 8 lb/gal EC, source unspecified) at 2.5 lb ai/A, and atrazine (AAtrex, 80% WP, source unspecified) at 4.0 lb ai/A, was applied preemergence on May 10, 1977 to field plots (360 ft^2) located in Maryland, and planted to corn. The test soil was a sandy loam with 1.5% organic matter. Soil samples (0-6 inches) were taken 0, 62, 124, and 220 days posttreatment from both treated and control plots.

Soil samples were analyzed for glyphosate and aminomethylphosphonic acid according to Monsanto Company's "Analytical residue method for N-phosphonomethylglycine and aminomethylphosphonic acid in forages, grains, soils, and water, Method C, Oct. 1, 1975", described in Study 11 (00108176). Recoveries from soil samples fortified with unspecified amounts of glyphosate and aminomethylphosphonic acid were 70 and 62%, respectively. The detection limit of both glyphosate and its degradate was 0.05 ppm.

REPORTED RESULTS:

The dissipation of glyphosate from a sandy loam soil, when applied alone or in combination with metolachlor and atrazine, is presented in Table 1. Aminomethylphosphonic acid was detected at a maximum concentration of 0.15 ppm, 124 days postreatment, in the plot treated with glyphosate alone. Neither glyphosate nor aminomethylphosphonic acid were detected in the control plot samples.

DISCUSSION:

1. Soil characteristics data did not include pH, textural analysis, and CEC.

2. Pretreatment soil samples were not submitted and immediate posttreatment samples showed the concentrations of glyphosate as ~29% of the applied.

3. Complete field test data, including depth of water table, slope of test site, rainfall, and air and soil temperature data, were not reported.

Table 1. Glyphosate and aminomethylphosphonic acid concentrations (ppm)[a] in a sandy loam soil in Maryland, treated with glyphosate alone, or in a combination tank mix of glyphosate (4 lb/gal EC), metolachlor (8 lb/gal EC), and atrazine (80% WP).[b]

Sampling interval (days)	Cumulative rainfall (inches)	Glyphosate	Aminomethylphosphonic acid
		Glyphosate	
0	--	0.59	ND[c]
62	2.6	0.20	ND
124	6.2	0.24	0.15
220	14.7	0.13	ND
		Glyphosate in combination with atrazine and metolachlor	
0	--	0.57	ND
62	2.6	0.33	0.10
124	6.2	0.47	ND
220	14.7	0.63	ND

[a] Values were corrected for recoveries and soil moisture contents.

[b] Treatment rates were 2.5, 2.0, and 4.0 lb ai/A for metolachlor, atrazine, and glyphosate, respectively.

[c] Not detected; detection limit was 0.05 ppm.

MATERIALS AND METHODS:

Glyphosate (Roundup, test substance uncharacterized, source unspecified), at 5 lb ai/A, alone and in combination with alachlor (Lasso, test substance uncharacterized, source unspecified) at 4.0 lb ai/A, and cyanazine (test substance uncharacterized, source unspecified) at 4.0 lb ai/A, was applied, in methanol or ammonium bicarbonate, to Drummer silty clay loam and Spinks loamy sand soils (5000-9000 kg). The test soils are characterized in Table 1. The treated soils were mixed, added to bread pans (soil depth was 2 inches), and placed in the greenhouse. The soils were sub-irrigated with deionized water, and kept under a 12-hr photoperiod. Soil samples were taken 0, 1.5, 3, 6, 12, and 24 weeks posttreatment.

Soil samples were analyzed for glyphosate and the glyphosate degradate aminomethylphosphonic acid as described in Monsanto Company's (1974) Pesticide Petition 5F1536. This method was not described. Recoveries from soil samples fortified with unspecified amounts of glyphosate and aminomethylphosphonic acid averaged 68 and 75%, respectively. The detection limit of both parent and degradate was not reported.

REPORTED RESULTS:

Average day and night temperatures were approximately 30 and 25 F, respectively.

The dissipation of glyphosate, when applied alone or in combination with alachlor and cyanazine, from loamy sand and silty clay loam soils, is presented in Table 2. Glyphosate dissipated from the loamy sand and silty clay loam soils with half-lives of <1.5 and ~3 weeks, respectively, when applied alone. In combination with simazine and alachlor, glyphosate dissipated from both soils with half-lives of 1.5-3.0 weeks. Aminomethylphosphonic acid was detected at maximum concentrations of 4.3 and 2.5 ppm six weeks posttreatment in the sandy loam and silty clay loam soils, respectively. No discernible differences in the dissipation of glyphosate or the rate of formation and decline of aminomethylphosphonic acid were observed when glyphosate was applied alone or in combination with alachlor and cyanazine.

DISCUSSION:

1. The test substance was not characterized.

2. Soil characteristics data did not include CEC. The test soil, reported to be Spink's sandy loam, is a loamy sand according to the USDA textural class.

3. The low recovery values for glyphosate and aminomethylphosphonic acid from fortified soil samples indicate considerable interferences may have occurred during analyses and results may not be accurate.

4. The analytical methods were not described.

Table 1. Soil characteristics.

Soil type	Sand	Silt	Clay	Organic matter	pH
			%		
Drummer silty clay loam	2.5	71.3	26.2	5.6	6.2
Spinks loamy sand	76.9	18.2	4.9	2.3	4.7

Table 2. Glyphosate and aminomethylphosphonic acid concentrations (ppm)[a] in loamy sand and silty clay loam soils treated with glyphosate alone, or in a combination tank mix of glyphosate, alachlor, and cyanazine.[b]

Sampling interval (weeks)	Drummer silty clay loam		Spinks loamy sand	
	Glyphosate	Aminomethylphosphonic acid	Glyphosate	Aminomethylphosphonic acid
		Glyphosate		
0	11.3	0.4	14.1	1.0
1.5	4.7	1.8	4.4	3.1
3	5.1	--[c]	1.9	3.8
6	1.7	2.4	1.7	4.3
12	0.9	1.6	0.5	3.0
24	0.4	1.0	0.2	2.3
	Glyphosate in combination with cyanazine and alachlor			
0	14.0	0.6	11.5	0.5
1.5	7.6	1.8	10.1	1.6
3	5.0	1.5	4.0	3.0
6	1.9	2.5	4.0	3.1
12	0.8	1.7	3.1	3.3
24	0.2	1.2	0.7	2.5

[a] Values were corrected for recoveries and soil moisture contents.

[b] Treatment rates were 4.0, 4.0, and 5.0 lb ai/A for alachlor, cyanazine, and glyphosate, respectively.

[c] Illegible.

CASE GS0178 GLYPHOSATE STUDY 14 PM 25 06/16/83

CHEM 103601 Isopropylamine Glyphosate

BRANCH EFB DISC 30 TOPIC

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00039381-A. CONTENT CAT 01

Kramer, R.M. 1975. Residues and persistence of glyphosate applied to a dry irrigation ditch. In Determination of residues of glyphosate and its metabolite in aquatic use of Roundup herbicide.

SUBST. CLASS = S.

DIRECT RVW TIME = 7 (MH) START-DATE END DATE

REVIEWED BY: W. Frantz
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CONCLUSIONS:

Field Dissipation - Aquatic and Aquatic Impact Uses

1. This study is scientifically valid.

2. Neither glyphosate nor aminomethylphosphonic acid were detected (<2.5 ppb) in two canal waters flooded ~6 months following treatment of glyphosate (test substance uncharacterized), at 5 lb ai/A, to two earthen-bottom dry canals located in Washington. Soil samples taken the day before the canals were filled (~6 months posttreatment) contained ~0.35 and 0.8 ppm glyphosate and aminomethylphosphonic acid, respectively, in each canal.

3. This study would not fulfill EPA Data Requirements for Registering Pesticides because the test substance was not characterized, soil samples were not characterized, complete water characteristics were not reported, rainfall data were not presented, and the formation and decline of degradates other than aminomethylphosphonic acid was not addressed.

MATERIALS AND METHODS:

One-half mile sections of two earthen-bottom dry irrigation canals located in Prosser, Washington (Canal A and Canal B), were treated with glyphosate (test substance uncharacterized, source unspecified), at 5 lb ai/A, on October 14, 1972. The canals were filled with water in the spring of 1973. Canal and water characteristics are presented in Table 1. Sampling stations were set-up 100 feet upstream from the treated site, and at 880, 1760, 2640, 5280, and 7920 feet downstream from the upper end of the treated area. Water samples (1 pint) were collected when the water front reached each station and subsequently at 15, 30, 45, 60, 90, 120, and 240 minutes. The sampling station located 2,640 feet downstream from the treatment site was sampled additionally at 8, 12, 24, and 48 hours.

Water samples were collected in polyethylene bottles from a median canal water depth. Soil samples (4-inch sampling depth) were collected from the banks of the canals at 260-foot intervals before and 1 day after treatment, and again in March before flooding the canals. Water and soil samples were analyzed for glyphosate and aminomethylphosphonic acid according to Monsanto Agricultural Research Report No. 325, described in Study 17 (00039381-C). The limit of detection was 2.5 ppb for both compounds. Recovery from water samples fortified with glyphosate at 2.5-100 ppb averaged 81.5%. Water samples fortified with aminomethylphophonic acid at 2.5-20 ppb ranged form 59-98%.

REPORTED RESULTS:

Average water temperatures for Canals A and B were 53 and 50 F, respectively.

Glyphosate and aminomethylphosphonic acid were not detected (<2.5 ppb) in any water samples. Soil samples taken the day before the canals were filled (~6 months posttreatment) contained ~0.35 and 0.8 ppm glyphosate and aminomethylphosphonic acid, respectively, in each canal. Neither parent nor degradate were detected in control water samples.

DISCUSSION:

1. The test substance was not characterized.

2. Soil sample characteristics, such as textural analysis, pH, organic matter content, and CEC, were not presented. In addition, water characteristics such as oxygen content and suspended solids were not reported.

3. Rainfall data were not reported.

4. Recovery values of glyphosate and aminomethylphosphonic acid from fortified soil samples were not reported.

5. Although soil samples were taken pretreatment and 1-day postreatment, no data were presented for these sampling intervals.

CASE GS0178 GLYPHOSATE STUDY 15 PM 25 06/16/83

CHEM 103601 Isopropylamine glyphosate

BRANCH EFB DISC 30 TOPIC 050525 GUIDELINE 40 CFR 163.62-9b/c/d

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00023979 CONTENT CAT 01

Monsanto Company. 19??. The soil dissipation of glyphosate, alachlor and simazine herbicides. Unpublished study received Dec. 19, 1977 under 524-285; CDL:232519-F.

SUBST. CLASS = S.

DIRECT RVW TIME = 5 (MH) START-DATE END DATE

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CONCLUSION:

Dissipation - Combination Products and Tank Mix Uses

This study could not be validated because the analytical methods were not described. Currently, data requirements for combination products and tank mix uses are not being imposed for this Standard.

MATERIALS AND METHODS:

Glyphosate (Roundup, test substance uncharacterized, source unspecified), at 5 lb ai/A, alone and in combination with alachlor (Lasso, test substance uncharacterized, source unspecified) at 4.0 lb ai/A, and simazine (test substance uncharacterized, source unspecified) at 4.0 lb ai/A, was applied, in methanol or ammonium bicarbonate, to Drummer silty clay loam and Spinks loamy sand soils (5000-9000 kg). The test soils are characterized in Table 1. The treated soils were mixed, added to bread pans (soil depth was 2 inches), and placed in the greenhouse. The soils were subirrigated with deionized water, and kept under a 12-hr photoperiod. Soil samples were taken 0, 1.5, 3, 6, 12, and 24 weeks posttreatment.

Soil samples were analyzed for glyphosate and the glyphosate degradate aminomethylphosphonic acid as described in Pesticide Petition 5F1536. This method was not reported. Recoveries from soil samples fortified with unspecified amounts of glyphosate and aminomethylphosphonic acid averaged 68 and 75%, respectively. The detection limit of both parent and degradate was not reported.

REPORTED RESULTS:

Average day and night temperatures were approximately 30 and 25 F, respectively.

The dissipation of glyphosate, when applied alone or in combination with alachlor and simazine, from loamy sand and silty clay loam soils, is presented in Table 2. Glyphosate dissipated from the loamy sand and silty clay loam soils with half-lives of <1.5 and ~3 weeks, respectively. Aminomethylphosphonic acid was detected at maximum concentrations of 4.2 and 2.4 ppm six weeks posttreatment in the loamy sand and silty clay loam soils, respectively.

DISCUSSION:

1. Soil characteristics data did not include CEC. The test soil, reported to be Spink's sandy loam is a loamy sand according to the USDA textural classification system.

2. The test substance was not characterized.

3. The low recovery values for glyphosate and aminomethylphosphonic acid from fortified soil samples indicate considerable interferences may have occurred during analyses and results may not be accurate.

4. The analytical methods were not described.

Table 1. Soil characteristics.

Soil type	Sand	Silt	Clay	Organic matter	pH
			%		
Drummer silty clay loam	2.5	71.3	26.2	5.6	6.2
Spinks loamy sand	76.9	18.2	4.9	2.3	4.7

Table 2. Glyphosate and aminomethylphosphonic acid concentrations (ppm)[a] in loamy sand and silty clay loam soils treated with glyphosate alone, or in a combination tank mix of glyphosate, alachlor, and simazine.[b]

Sampling interval (weeks)	Drummer silty clay loam		Spinks loamy sand	
	Glyphosate	Aminomethylphosphonic acid	Glyphosate	Aminomethylphophonic acid
		Glyphosate		
0	10.5	0.3	13.5	0.9
1.5	4.4	1.8	3.9	2.9
3	5.0	1.6	1.9	3.8
6	1.7	2.4	1.6	4.2
12	0.9	1.6	0.5	3.0
24	0.4	1.0	0.2	2.3
		Glyphosate in combination with simazine and alachlor		
0	15.9	0.4	13.7	0.4
1.5	5.4	1.8	9.6	2.1
3	3.8	1.7	2.9	3.8
6	1.3	2.0	1.7	3.4
12	0.5	1.6	0.7	2.6

[a] Values were corrected for recoveries and soil moisture contents.

[b] Treatment rates were 4.0, 4.0, and 5.0 lb ai/A for alachlor, simazine, and glyphosate, respectively.

CASE GS0178 GLYPHOSATE STUDY 16 PM 25 06/16/83

CHEM 103601 Isopropylamine glyphosate

BRANCH EFB DISC 30 TOPIC 100520

FORMULATION 12 - EMULSIFIABLE CONCENTRATE (EC OR E)

FICHE/MASTER ID 00017704 CONTENT CAT 02

Kern, C.L. and D. Staniforth. 1978. Metolachlor (Dual 8E) + atrazine (AAtrex) + Glyphosate (Roundup 4E): AG-A No. 4780 I-II. Unpublished study received Jan. 4, 1980 under 100-583; prepared in cooperation with Iowa State Univ. and ADC Laboratories, submitted by Ciba-Geigy Corp., Greensboro, NC; CDL:241545-L.

SUBST. CLASS = S.

DIRECT RVW TIME = 9 1/2 (MH) START-DATE END DATE

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CONCLUSION:

Dissipation - Combination Products and Tank Mix Uses

This study is scientifically invalid because the data were too variable to accurately assess the dissipation of glyphosate from soil when applied alone or in combination with atrazine and metolachlor. Currently, data requirements for combination products and tank mix uses are not being imposed for this Standard.

MATERIALS AND METHODS:

Glyphosate (Roundup, 4 lb/gal EC, source unspecified), at 4 lb ai/A, alone and in combination with metolachlor (Dual, 8 lb/gal EC, source unspecified) at 2.5 lb ai/A, and atrazine (AAtrex, 80% WP, source unspecified) at 4.0 lb ai/A, was applied preemergence with nitrogen fertilizer (28% N) on May 16, 1977 to field plots (300 ft^2) located in Iowa, and planted to corn. The test soil was a silty clay loam (pH 6.5, organic matter content 5.0%). Soil samples (0-6 inches) were taken 0, 31, 61, 123, and 319 days posttreatment.

Soil samples were analyzed for glyphosate and aminomethylphosphonic acid according to Monsanto Company's "Analytical Residue Method for N-Phosphonomethylglycine and Aminomethylphophonic Acid in Forages, Grains, Soils, and Water, Method C, Oct. 1, 1975", described in Study 11 (00108176). Average recoveries from soil samples fortified with unspecified amounts of aminomethylphosphonic acid and glyphosate were 58% for the degradate and ranged from 40-58% for glyphosate. The detection limit of both glyphosate and degradate was 0.05 ppm.

REPORTED RESULTS:

The dissipation of glyphosate, when applied alone or in combination with metolachlor and atrazine, from a sandy loam soil in Iowa, is presented in Table 1. Aminomethylphosphonic acid was detected at a maximum concentration of 0.21 ppm 31 days postreatment in the plot treated with glyphosate alone. Aminomethylphosphonic acid was not detected in the control plot samples. Glyphosate was detected in control plot samples at a concentration of <0.06 ppm.

DISCUSSION:

1. Soil characteristics data did not include CEC and textural analysis.

2. Pretreatment soil samples were not submitted, and immediate posttreatment samples showed the concentrations of glyphosate as ~6.5 to 21% of the applied. All data were corrected for recovery values.

3. The low recovery values for glyphosate and aminomethylphosphonic acid from fortified soil samples indicate considerable interferences may have occurred during analyses and results may not be accurate.

4. Complete field test data, including depth of water table, slope of test site, and soil temperature data, were not reported. Rainfall and air temperature data for the first and second half of the experiment were presented only as above average, average, or below average.

Table 1. Glyphosate and aminomethylphosphonic acid concentrations (ppm)[a] in a silty clay loam soil in Iowa, treated with glyphosate alone or in a combination tank mix of glyphosate (4 lb/gal), metolachlor (8 lb/gal), and atrazine (80% WP).[b]

Sampling interval (days)	Glyphosate	Aminomethylphosphonic acid
	Glyphosate	
0	0.13	ND[c]
31	0.14	0.21
61	0.13	0.17
123	0.23	0.06
391	ND	0.07
	Glyphosate in combination with atrazine and metolachlor	
0	0.42	ND
31	0.11	0.17
61	0.19	0.17
123	0.16	0.09
391	ND	0.10

[a] Values were corrected for recoveries and soil moisture contents.

[b] Treatment rates were 2.5, 2.0, and 4.0 lb ai/A for metolachlor, atrazine, and glyphosate, respectively.

[c] Not detected; detection limit is 0.05 ppm.

CASE GS0178 GLYPHOSATE STUDY 17 PM 25 06/16/83

CHEM 103601 Isopropylamine glyphosate

BRANCH EFB DISC 30 TOPIC

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00039381-C CONTENT CAT 02

Edwards, W.M. 1975. Field runoff of glyphosate from Coshocton watersheds. In Determination of residues of glyphosate and its metabolite in aquatic use of Roundup herbicide.

SUBST. CLASS = S.

DIRECT RVW TIME = 8 (MH) START-DATE END DATE

REVIEWED BY: W. Frantz
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CONCLUSION:

Mobility - Leaching and Adsorption/Desorption

This runoff study could not be validated because pretreatment and immediate posttreatment soil samples were not analyzed to confirm glyphosate application rates. In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides because the method was not one of the three (i.e., soil TLC, soil columns, batch equilibrium) recommended for determining pesticide mobility in soils, complete soil characteristics were not presented, and the formulation of the test substance was not reported.

MATERIALS AND METHODS:

Ohio Watersheds 103 (0.65 A, silt loam soils with 11.3% slope, alfalfa-orchardgrass cover) and 123 (1.37 A, silt loam soils with 5.8% slope, no-till corn cover) were treated on April 18 and April 27, 1973, respectively, with glyphosate (Roundup, MON 2139, 3 lb/gal, formulation and source unspecified), at 3 lb ai/A. Runoff samples were collected on April 27, May 10, June 4, 6, and 17, August 14, October 8, and October 31. Soil samples (0- to 2-inch sampling depth) were taken pretreatment from Watersheds 103 and 123 on April 30 and May 9, respectively, and thereafter from both Watersheds on June 14, July 9, and August 6.

Glyphosate and the degradate aminomethylphosphonic acid were determined in the runoff water by passing the water through anion and cation exchange columns to clean up the samples and separate the parent from the degradate. The parent and degradate were then acylated with trifluoroacetic acid and trifluoroacetic anhydride, and methylated with diazomethane. The glyphosate and aminomethylphosphonic acid derivatives were quantified by GC using a flame photometric detector. Recovery values for six water samples fortified with glyphosate at 2.5 or 5.0 ppb ranged from 55.7 to 100% and from 49.2 to 100%, respectively. The detection limit was 2.5 ppb. Recovery values for aminomethylphosphonic acid ranged from 54.9 to 94.8% and from 57.3 to 98.8%, respectively, for water samples fortified with 2.5 and 5.0 ppb.

REPORTED RESULTS:

Less than 0.2% of the applied, for both sites, was detected in the runoff (Table 1). Of the glyphosate detected in the runoff from both sites, essentially 100% of the recovered was detected in the first two runoff events. Aminomethylphosphonic acid was detected at a maximum concentration of 27 and 19 ppb from the first runoff events of Watersheds 103 and 123, respectively.

DISCUSSION:

1. Because pretreatment and immediate postapplication soil samples were not analyzed, the extent of glyphosate mobility in runoff could not be accurately assessed.

2. It was reported that soil samples were collected, but glyphosate and aminomethylphosphonic acid concentration data in soil were not reported.

3. The method was not one of the three (i.e., soil TLC, soil columns, batch equilibrium) recommended for determining pesticide mobility in soils.

4. Complete soil characteristics, including textural analysis, pH, organic matter content, and CEC, were not reported.

5. The recoveries of glyphosate and aminomethylphosphonic acid from fortified water samples varied from 49 to 100% and and 55 to 98%, respectively. It was not reported whether data were corrected for recoveries.

Table 1. Glyphosate and aminomethylphosphonic acid concentrations (ppb) in runoff water of two Ohio watersheds following treatment with glyphosate (Roundup, 3 lb/gal) at 3 lb ai/A.

Sampling interval (days)	Runoff collected (liters)	Glyphosate (ppb)	Glyphosate (% of applied)	Degradate[a] (ppb)
		Ohio Watershed 103		
9	9,208	70	0.09	27
22	30,985	12	0.05	<10
47	2,873	5	0.002	8
49	7,751	3	0.00	7
60	1,617	4	--	<4
118	635	ND[c]	--	ND[c]
Total	53,069[b]		<0.15	
		Ohio Watershed 123		
10	37,871	73	0.15	19
35	2,620	11	0.002	12
37	2,690	4	<0.001	7
48	14,577	ND	--	ND
106	1,100	ND	--	ND
160	1,100	ND	--	ND
184	11,042	ND	--	ND
Total	71,000		<0.16	

[a] Aminomethylphosphonic acid.

[b] Equivalent runoff volume = 0.794 inches.

[c] Not detected; detection limit was 2.5 ppb.

[d] Equivalent runoff volume = 0.504 inches.

CASE GS0178 GLYPHOSATE STUDY 18 PM 25 06/16/83

CHEM 103601 Isopropylamine glyphosate

BRANCH EFB DISC 30 TOPIC

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00039381-C CONTENT CAT 0

Sleight III, B.H. 1975. Exposure of fish to Roundup, accumulation, distribution, and elimination. In Determination of residues of glyphosate and its metabolite in aquatic use of Roundup herbicide.

SUBST. CLASS = S.

DIRECT RVW TIME = 7 (MH) START-DATE END DATE

REVIEWED BY: W. Frantz
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SIGNATURE: W. Frantz DATE: Apr. 17, 1985

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SIGNATURE: DATE:

CONCLUSION:

Laboratory Accumulation - Fish

This study could not be validated because insufficient data were presented to support the reported results. In addition, this study would not fullfill EPA Data Requirements for Registering Pesticides because the purity of the test substance was not reported, radioactive residues were not characterized, cumulative fish mortality was not reported, and radioactive residues in viscera, whole-body tissue, and exposure water, were not provided.

MATERIALS AND METHODS:

Bluegill sunfish (Lepomis macrochirus; average length and weight 42 mm and 1.3 g, respectively) were maintained for 30 days, at unspecified conditions, prior to test initiation. Flow-through aquatic exposure systems were prepared using three 30-l aquaria equipped with continuous flow-through proportional dilution apparutus, as described by Mount and Brunge [1967. Water Res. (1) 21-24]. Aerated well water [pH 7.3, total hardness ($CaCO_3$) 40 ppm, dissolved oxygen >5.0 ppm, temperature 21 ±1 C] was provided to each aquarium at a flow rate of 5 l/hr (4 turnovers/day). Bluegill (100) were placed in each aquarium. Two aquariums were continuously treated with [^{14}C]glyphosate (CP 67573, specific activity 86 µCi/mg, purity and source unspecified), at 0.005 and 0.625 ppm. The third aquarium served as an untreated control.

Water and fish samples were taken at 1, 3, 7, 10, 14, 21, and 28 days of exposure. After the 28-day exposure period, fish remaining in the treated aquariums were transferred to aquariums containing untreated water for 14 days of depuration.

Water samples (500 ml) were concentrated on a rotary evaporator to <10 ml, diluted with distilled water to 25 ml, and quantified using LSC. Fish (5) were eviscerated, the edible tissue combusted, the evolved $^{14}CO_2$ trapped in ethanolamine, and quantified using LSC. The recovery values ranged from 98 to 100%. Detection limits in fish and and water exposed to the lower (0.005 ppm) and higher (0.612 ppm) treatment rates were 0.01 and 0.001, and 1.0 and 0.005 ppm, respectively. The recovery value in water was 84%.

REPORTED RESULTS:

Cumulative fish mortality during the test period was not reported; however, the fish were reported to have been in excellent physical condition. Pretreatment fish mortality was <1%. [^{14}C]Glyphosate residues in the edible tissue of bluegill sunfish accumulated to maximum concentrations of <1.13 and 0.011 ppm on day 28 of exposure when exposed to average [^{14}C]glyphosate concentrations of 0.61 and 0.005 ppm, respectively (Table 1). Radioactive residues accumulated during the 14-day depuration period in both treatments. Maximum concentrations of [^{14}C]glyphosate residues exposed to 0.612 and 0.005 ppm occurred at day 7 (3.07 ppm) and day 10 (0.031 ppm) of depuration, respectively. After 28 days of exposure to 0.005 and 0.612 ppm [^{14}C]-glyphosate, average radioactivity detected in the visceral tissue of bluegill sunfish was 0.24 and 11.1 ppm, respectively.

DISCUSSION:

1. Radioactive residues were not characterized.

2. The purity of the test substance was not reported.

3. Radioactive residues in whole-body tissues were not provided, and were incompletely provided for visceral tissue.

4. Cumulative fish mortality was not reported.

5. [^{14}C]Glyphosate concentrations in water were not presented at any individual sampling interval. Concentrations were, instead, expressed as an average value for the whole experiment.

6. The increase in ^{14}C residues in the edible tissue during depuration was attributed to a redistribution of ^{14}C residues within the fish. Without data on ^{14}C residues in visceral tissue during the depuration period, this explanation could not be substantiated.

Table 1. [^{14}C]Glyphosate residues (ppm) in the edible tissue of bluegill sunfish during a 28-exposure period, to [^{14}C]glyphosate at 0.612 and 0.005 ppm, and a 14-day depuration period.

	Sampling interval (days)	Application rate			
		0.612[a] ppm	BCF[b]	0.005[a] ppm	BCF[b]
Exposure	1	1.02 (0.34)[c]	1.7	ND	
	3	<1.01 (0.27)	1.6	0.01	2.0
	7	ND		ND	
	10	ND		ND	
	14	ND		<0.011 (0.002)	2.2
	21	ND		ND	
	28	<1.13 (0.13)	1.9	0.011 (0.0088)	2.2
Depuration	1	2.31 (0.36)	3.8	0.022 (0.003)	4.4
	3	1.59 (0.24)	2.1	0.022 (0.005)	4.4
	7	3.07 (5.00)	5.0	0.020 (0.006)	4.0
	10	1.20 (0.22)	2.0	0.031 (0.010)	6.2
	14	2.08 (0.47)	3.4	0.16 (0.003)	3.2

[a] Average measured concentrations.

[b] Bioconcentration factor (BCF) = $\frac{\text{concentration in fish tissue}}{\text{avg. concentration in water}}$.

[c] Average (± SD) based on 10 radiometric analyses.

CASE GS0178 GLYPHOSATE STUDY 19 PM 25 06/16/83

CHEM 103601 Isopropylamine glyphosate

BRANCH EFB DISC 30 TOPIC 051025 GUIDELINE 40 CFR 163.62-10c

FORMULATION 15 - SOLUBLE CONCENTRATE

FICHE/MASTER ID 00108173 CONTENT CAT 01

Monsanto Co. 1978. Residue studies for use of Roundup herbicide in aquatic situations. Compilation; unpublished study received Dec. 27, 1978 under 524-308; CDL:097760-A; 097761; 097762).

SUBST. CLASS = S.

DIRECT RVW TIME = 8 (MH) START-DATE END DATE

REVIEWED BY: G. Moore
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CONCLUSION:

Laboratory Accumulation - Fish

This study is scientifically invalid because the sampling protocol was inadequate to assess the accumulation of glyphosate in fish. In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides because a flow-through exposure system was not used, the test organisms were incompletely described, and the accumulation period was not long enough.

MATERIALS AND METHODS:

Twenty-five channel catfish (Ictalurus punctatus, 15.4 g/fish average weight) were introduced into a 60-l aquaria of well water (pH 7.5, temperature 22 C, dissolved oxygen 7 mg/l, total hardness as calcium carbonate 250 mg/l) with a static concentration of N-phosphonomethyl-labeled [^{14}C]glyphosate (specific activity 10.12 mC/mM, 94% pure, source unspecified) at 1.0 ppm. A similar system was established with untreated water to serve as a control.

Water samples were taken at day 1, 3, 7, and 10 posttreatment. Twenty fish were taken from the aquaria after 10 days of exposure. The remaining fish were placed in an untreated tank for a 14-day depuration period, after which they were sampled. Water samples were concentrated and spotted on microcrystalline cellulose TLC plates. The plates were developed with an aged (24 hours) solution containing disodium EDTA (1.2 g), 17 N ammonium hydroxide (100 ml), water (475 ml), 1-propanol (350 ml), 2-propanol(75 ml), isobutyric acid (2500 ml), and the radioactivity was quantified by beta camera analysis. Water samples were also analyzed by HPLC and LSC.

Fish tissue samples were extracted three times with distilled water. The extracted tissues were combusted and the radioactivity in both the combusted samples and aliquots of extracts was quantified by LSC. The water extracts were cleaned by methanol and ether extraction and analyzed by column chromatography for glyphosate and aminomethylphosphonic acid.

REPORTED RESULTS:

After exposure to [^{14}C]glyphosate at 1.0 ppm for 10 days, edible tissue, viscera, and whole fish accumulated 0.057, 0.25, and 0.014 ppm of [^{14}C]glyphosate. After depuration for 14 days, detectable concentrations had declined to 0.02, 0.076, and 0.047 ppm in edible tissue, viscera and whole fish, respectively. In all samples >86% of the detected radioactivity was identified as glyphosate, with the remainder being aminomethylphosphonic acid. No other degradates were detected. Total [^{14}C]glyphosate residues detected in water samples averaged 0.848 ± 0.02 ppm, of which >89% was identified as parent compound and the remainder as aminomethylphosphonic acid.

DISCUSSION:

1. The sampling protocol (two sampling intervals) was inadequate to assess the accumulation and depuration of glyphosate in fish.

2. A static, rather than a flow-through system was used. Consequently the fish may not have been exposed to a constant level of glyphosate.

3. The test organisms were not completely described (average length and mortality rate during acclimation were not reported).

4. Detection limits were not reported.

5. The accumulation period was not long enough (28 days is recommended) to assess the potential for glyphosate to accumulate in fish.

6. No data were reported for controls.

CASE GS0178 GLYPHOSATE STUDY 20 PM 25 06/16/83

CHEM 103601 Isopropylamine glyphosate

BRANCH EFB DISC 30 TOPIC 051025 GUIDELINE 40 CFR 163.62-10c

FORMULATION 15 - SOLUBLE CONCENTRATE

FICHE/MASTER ID 000108173-C CONTENT CAT 01

Monsanto Co. 1978. Residue studies for use of Roundup herbicide in aquatic situations. Compilation; unpublished study received Dec. 27, 1978 under 524-308; CDL:097760-A; 097761; 097762.

SUBST. CLASS = S.

DIRECT RVW TIME = 8 (MH) START-DATE END DATE

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CONCLUSION:

Laboratory Accumulation - Fish

This study is scientifically invalid because the experimental design was inappropriate to assess the accumulation of glyphosate in fish. In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides because the test substance was not characterized, and data were not reported for the water samples.

MATERIALS AND METHODS:

Experiment 1

Rainbow trout (Salmo gairdneri; average length 280 mm, average weight 134 g), channel catfish (Ictalurus punctatus; average length 290 mm, average weight 92 g), and largemouth bass (Micropterus salmoides; average length 190 mm; average weight 57 g) were introducted into fifteen 550-l fiberglass tanks equipped with continuous-flow proportional dilution apparatus as described by Mount and Brungs (1967. Water Res. (1) 21-24). Aerated well water (pH 7.1, total hardness as calcium carbonate 35 ppm, dissolved oxygen content >5 ppm, temperature 18 ± 1 C) was provided to each tank (160 l/hr). Four tanks for each species were treated with glyphosate (test substance uncharacterized, source unspecified) at either 0.1, 1.0, 3.0, or 10.0 ppm, with the fifth tank serving as a control.

Fish samples were taken from each tank on days 1, 3, 7, 10, and 14 of the exposure period. After the 14-day exposure period, the treated water was replaced with untreated water. Fish were sampled on days 3, 7, 14, 21, 28, and 35 of the depuration period. Water samples were taken on days 0, 2, 4, 6, 8, 10, 12, and 14 of the exposure period and on days 3, 7, 14, 21, 28, and 35 of the depuration period.

Fish were divided into edible and nonedible (head and viscera) portions and ground for analysis. The samples were extracted with chloroform and water and the extracts were cleaned up by eluting through resin columns with 0.5 M ammonium bicarbonate. The extracts were evaporated, dissolved in distilled water and separated by column chromatography. Fractions, containing glyphosate and aminomethylphosphonic acid, were evaporated and redissolved in trifluoroacetic acid. Methyl derivatives of glyphosate and aminomethylphosphonic acid, in the fractions were prepared and quantified using GLC with flame photometric detection. The detection limit for fish tissue was 0.05 ppm for both compounds. Recovery values ranged from 72 to 76% for glyphosate and from 71 to 77% for aminomethylphosphonic acid.

Experiment 2

Carp (species unspecified) and channel catfish (Ictalurus punctatus) were introducted into tanks equipped with continuous-flow proportional dilution, as described in Experiment 1. The fish were exposed to glyphosate (test substance uncharacterized) at 10.0 ppm and water and fish samples were taken and analyzed as previously described in Experiment 1.

REPORTED RESULTS:

Experiment 1

Glyphosate detected in rainbow trout, catfish and largemouth bass exposed at 0.1, 1.0, 3.0 and 10 ppm is shown in Table 1-3. No aminomethylphosphonic acid was detected in any of the tissue samples.

Experiment 2

Glyphosate and aminomethylphosphonic acid levels detected in carp and catfish exposed at 10.0 ppm are shown in Tables 4 and 5.

DISCUSSION:

1. Cumulative fish mortality during a 30-day acclimation period was <2%.

2. The exposure period (14 days) was not of sufficient duration to assess the accumulation of glyphosate in fish.

3. Although it was reported that water samples were taken, no analytical method was described and no data were presented. Consequently, bioaccumulation factors could not be calculated.

4. The test substance was not characterized.

Table 1. Glyphosate detected (ppm) in edible and visceral tissues of catfish exposed to 4 concentrations of glyphosate.

Sampling interval (days)	Glyphosate treatment rate (ppm)							
	0.1		1.0		3.0		10.0	
	Edible	Visceral[a]	Edible	Visceral	Edible	Visceral	Edible	Visceral
				Exposure				
1	--[b]	ND[c]	--	ND	--	ND	--	ND
3	ND	ND	ND	ND	0.06	ND	0.13	ND
7	ND	ND	0.05	ND	0.42	ND	0.55	0.57
10	ND	ND	0.13	ND	0.18	0.45	0.26	ND
14	ND	ND	ND	ND	0.11	ND	0.16	ND
				Depuration				
3	ND	ND	ND	ND	ND	ND	0.2	ND
7	ND	ND	ND	ND	ND	ND	0.08	ND
14	ND	ND	ND	ND	ND	ND	ND	ND
21	ND	ND	0.05	0.12	0.16	0.16	0.12	0.26
28	0.10	ND	ND	ND	ND	ND	0.07	ND
34	ND	ND	ND	ND	ND	0.07	0.07	0.21

[a] Includes fish heads.

[b] Not sampled.

[c] Not detected; detection limit was 0.05 ppm.

Table 2. Glyphosate detected (ppm) in edible and visceral tissues of largemouth bass exposed to 4 concentrations of glyphosate.

Sampling interval (days)	Glyphosate treated rate (ppm)							
	0.1		1.0		3.0		10.0	
	Edible	Visceral[a]	Edible	Visceral	Edible	Visceral	Edible	Visceral
				Exposure				
1	--[b]	ND[c]	--	ND	--	ND	--	ND
3	ND	ND	ND	ND	ND	ND	ND	ND
7	ND	ND	ND	ND	ND	ND	0.08	ND
10	ND	ND	ND	ND	0.06	ND	0.10	ND
14	ND	ND	ND	ND	0.06	ND	0.14	0.13
				Depuration				
3	ND	ND	ND	ND	0.04	ND	0.12	ND
7	ND	ND	ND	ND	ND	ND	0.08	ND
14	ND	ND	ND	ND	ND	ND	ND	ND
21	ND	ND	0.08	ND	0.12	ND	0.24	0.16
28	ND	ND	ND	ND	ND	ND	ND	ND
35	ND	ND	ND	ND	ND	ND	ND	0.06

[a] Includes fish heads.

[b] Not sampled.

[c] Not detected; detection limit was 0.05 ppm.

Table 3. Glyphosate detected (ppm) in edible and visceral tissues of rainbow trout exposed to 4 concentrations of glyphosate.

Sampling interval (days)	Glyphosate treated rate (ppm)							
	0.1		1.0		3.0		10.0	
	Edible	Visceral[a]	Edible	Visceral	Edible	Visceral	Edible	Visceral
				Exposure				
1	--[b]	ND[c]	--	ND	--	ND	--	ND
3	ND	ND	ND	ND	ND	ND	0.06	ND
7	ND	ND	ND	ND	ND	ND	0.12	ND
10	ND	ND	ND	ND	0.11	ND	0.13	0.76
14	ND	ND	ND	ND	0.06	0.12	0.14	ND
				Depuration				
3	ND	ND	ND	ND	0.04	ND	0.06	ND
7	ND	ND	ND	ND	ND	ND	ND	ND
14	ND	ND	ND	ND	ND	ND	ND	ND
21	ND	0.04	0.04	0.06	0.10	0.07	0.12	0.16
28	ND	ND	ND	ND	ND	ND	ND	ND
35	ND	ND	ND	ND	ND	ND	ND	ND

[a] Includes fish heads.

[b] Not sampled.

[c] Not detected; detection limit was 0.05 ppm.

Table 4. Glyphosate and AMPA[a] detected (ppm) in the visceral[b] portion of carp and catfish exposed to glyphosate at 10.0 ppm.

Sampling interval (days)	Carp		Catfish	
	Glyphosate	AMPA	Glyphosate	AMPA
		Exposure		
1	0.36	ND[c]	0.44	ND
3	0.34	ND	0.99	ND
7	2.52	ND	2.22	0.10
10	3.96	0.12	1.80	ND
14	3.08	ND	2.17	0.05
		Depuration		
3	1.29	ND	0.58	ND
7	0.70	ND	1.88	0.16
14	0.22	ND	0.46	ND
21	0.14	ND	0.10	ND
28	0.06	ND	0.11	ND
35	ND	ND	0.18	ND

[a] Aminomethylphosphonic acid.

[b] Includes fish heads.

[c] Not detected; detection limits were 0.05 ppm.

Table 5. Glyphosate and AMPA[a] detected (ppm) in the edible portion of carp and catfish exposed to glyphosate at 10.0 ppm.

Sampling interval (days)	Carp		Catfish	
	Glyphosate	AMPA	Glyphosate	AMPA
1	0.08	ND[c]	ND	ND
3	0.16	ND	0.20	ND
7	0.28	ND	0.10	ND
10	0.28	ND	0.05	ND
14	0.41	ND	0.08	ND
3	0.12	ND	0.06	ND
7	0.10	ND	0.06	ND
14	0.06	ND	0.08	ND
21	ND	ND	ND	ND
28	ND	ND	ND	ND
35	ND	ND	ND	ND

[a] Aminomethylphosphonic acid.

[b] Not detected; detection limits were 0.05 ppm.

CASE GS0178 GLYPHOSATE STUDY 21 PM 25 06/16/83

CHEM 103601 Isopropylamine glyphosate

BRANCH EFB DISC 30 TOPIC 051025 GUIDELINE 40 CFR 163.62-10c

FORMULATION 15 - SOLUBLE CONCENTRATE

FICHE/MASTER ID 00108173-E CONTENT CAT 01

Monsanto Co. 1978. Residues for use of Roundup herbicide in Aquatic Situations. Compilation; unpublished study received Dec. 27, 1978 under 524-308; CDL:097760-A; 097761; 097768.

SUBST. CLASS = S.

DIRECT RVW TIME = 7 (MH) START-DATE END DATE

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CONCLUSIONS:

Laboratory Accumulation - Fish

1. This study is scientifically valid.

2. [^{14}C]Glyphosate residues (uncharacterized) accumulated in the whole-body tissue of marsh clams with a maximum bioconcentration factor of ~31x in a static exposure system containing N-phosphonomethyl-labeled [^{14}C]glyphosate (>97% pure). Only 25% of the accumulated [^{14}C]glyphosate residues were eliminated after a 21-day depuration period.

3. This study does not fullfill EPA Data Requirements for Registering Pesticides because radioactive residues were not characterized, radioactive residues in visceral and edible tissue were not analyzed, a flow-through exposure system was not used, and the experiment was not conducted using fish.

MATERIALS AND METHODS:

Duplicate model aquatic ecosystems were prepared by adding 10 kg of Spinks sandy loam soil (75.1%, sand, 17.8% silt, 4.8% clay, 2.4% organic matter content, pH 4.7) to two Teflon-lined, stainless steel tanks to a depth of 2.5 cm. One tank served as a control. The soil was treated with N-phosphonomethyl-labeled [^{14}C]glyphosate (purity >97%, specific activity 2,026 dpm/µg, Monsanto Agricultural Products Division), at 4 lb ai/A, and incubated under a 9 hour fluorescent light:15 hour dark photoperiod for 5 days. After the aging period, 7 l of 7 ppt sea water (dissolved oxygen content 6.3-9.0 mg/l) were added to each tank to a depth of 2.5 cm above the soil, and the submerged treated soil was incubated for another 25 days. At the end of this incubation period, the tanks were filled with ~120 l of sea water. Three days later 100 marsh clams (Rangia cueanta, 0.74 ± 0.24 g average weight) were introduced into each system. Cumulative mortality for the clams during a 30-day acclimation period prior to the initiation of the study was <2%.

Following treatment, soil samples were taken on days 1, 5, 6, 15, and 33. Soil, water, and clams remaining in each tank after the 35-day exposure period were depurated for 21 days in untreated water. Samples of clams during period were taken on days 1, 3, 7, 10, 14, and 21.

Radioactivity in triplicate 1-ml water samples was quantified directly using LSC. Soil samples (size unspecified) were air-dried for 24 hours, combusted, the evolved $^{14}CO_2$ trapped and quantified using LSC. Five clams were removed at each sampling interval, air-dried for 24 hours, combusted, and the $^{14}CO_2$ evolved was trapped and quantified using LSC. Recovery values for radioassays ranged from 99 to 101%. The detection limits were 0.006-0.025 ppm for clam samples. Detection limits and recovery values for water were not reported.

REPORTED RESULTS:

The calculated maximum bioconcentration factor for [^{14}C]glyphosate residues in the whole-body tissue of marsh clams was ~31x on day 28 of exposure (Table 1). Approximately 25% of the accumulated [^{14}C]glyphosate residues were eliminated by day-21 of the depuration period. The mean concentration of [^{14}C]glyphosate residues in water during the 35-day exposure period was 0.028 ± 0.014 ppm, ranging from 0.013 to 0.056 ppm.

No clam mortality occurred during the test period, and the clams were reported to have been in excellent physical condition.

DISCUSSION:

1. Radioactive residues were not characterized.

2. A static rather than a flow-through system was used, therefore, the test organisms were not exposed to a constant concentration of glyphosate.

3. Radioactive residues in viscera and edible tissues were not analyzed.

4. Detection limits and recovery values for water were not reported.

Table 1. [^{14}C]Glyphosate residues (ppm) in soil, water, and whole-body tissue of marsh clams during a static accumulation study.

	Sampling interval (days)	Clams (ppm)	BCF[a]	Water (ppm)	Soil (ppm)
Pre-exposure	1				37
	5				40
	6				24
	15				26
	33				7.7
Exposure	1	0.18	14	0.013	6.0
	3	0.15	5.6	0.027	9.3
	7	0.25	7.4	0.034	8.0
	10	0.30	7.7	0.039	12.0
	14	0.27	4.8	0.056	8.7
	21	0.52	25	0.021	11.0
	28	0.44	31	0.014	13.0
	35	0.54	23	0.023	11.0
Depuration	1	0.59			
	3	0.40			
	7	0.38			
	10	0.48			
	14	0.45			
	21	0.43			

[a] Bioconcentration factor (BCF) = $\frac{\text{concentration in clam tissue}}{\text{concentration in water}}$.

CASE GS0178 GLYPHOSATE STUDY 22 PM 25 06/16/83

CHEM 103601 Isopropylamine glyphosate

BRANCH EFB DISC 30 TOPIC

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00039381-D CONTENT CAT 01

Comes, R.D. 1975. Residues and persistence of glyphosate in irrigation water. In Determination of residues of glyphosate and its metabolite in aquatic use of Roundup herbicide.

SUBST. CLASS = S.

DIRECT RVW TIME = 8 (MH) START-DATE END DATE

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CONCLUSION:

Field Dissipation - Aquatic and Aquatic Impact Uses

This study is scientifically invalid because the recovery of glyphosate from fortified water samples was too variable to accurately assess the dissipation of glyphosate from flowing irrigation canal water. In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides because the test substance was not characterized, soil samples were not analyzed, complete field test data were not reported, and the formation and decline of degradates other than aminomethylphosphonic acid was not addressed.

MATERIALS AND METHODS:

Five- and nine-mile earthen bottom irrigation canals, located in Prosser, Washington, were treated with glyphosate (test substance uncharacterized, source unspecified), at 150 ppb. Approximately 1 mile of flowing irrigation water was treated by metering the test substance into the canals, and marking the treated water with a dye. The canal water characteristics are presented in Table 1. Sampling stations were located upstream from the treated site, and downstream at 0.2 and 1.0 mile, and thereafter at 2-mile increments. Eight water samples were taken at each sampling station downstream from the application site. The first sample commenced as the dye started past the sampling station, and the last sample was taken immediately after the end of the dye had past the sampling station.

Water samples were analyzed for glyphosate and the degradate aminomethylphosphonic acid as described in Study 17 (00039381-C). Recovery values for water samples fortified with 2.5-100 ppb glyphosate, from both canals, ranged from ~45 to 113%. Recovery values of water samples from the East Canal fortified with aminomethylphosphonic acid at 2.5-100 ppb ranged from 64 to 96%. Aminomethylphosphonic acid recoveries from water samples of the No. 4 Canal, when fortified with 2.5-5.0 ppb, ranged from 68 to 92%. The detection limit was 2.5 ppb for both parent and degradate.

REPORTED RESULTS:

Average water temperatures for the East Canal and No. 4 Canal were 54 and 48 F, respectively.

Glyphosate concentrations in irrigation water of the East Canal and No. 4 Canal, treated with glyphosate at 150 ppb, are presented in Table 2. Glyphosate concentrations slowly dissipated from both canals as the distance from the treatment site increased. Maximum concentrations of glyphosate in East Canal and No. 4 Canal were detected at the first sampling station (0.2 mile) downstream from the treatment site at 153 and 161 ppb, respectively. Glyphosate concentrations decreased to 119 ppb at the last sampling station (5 miles) in the East Canal, and to 90 ppb at the last sampling station (9 miles) in No. 4 Canal. Concentrations of aminomethylphosphonic acid were below the limit of detection (2.5 ppb) at all sampling intervals and stations for both canals. Neither parent nor degradate was detected (2.5 ppb) in the control (upstream) samples from either canal.

DISCUSSION:

1. The test substance was not characterized.

2. Soil samples were not analyzed.

3. The recovery of glyphosate from fortified water samples varied from 45 to 113% for the No. 4 Canal and from 62 to 95% for the East Canal. This much variability makes the dissipation of glyphosate from flowing irrigation water difficult to discern.

4. Complete water characteristics, including oxygen contents and percent suspended solids, were not presented. Additionally, soil characteristics of the canals, such as textural analysis, pH, organic matter contents, and CEC, were not reported.

Table 1. Water characteristics.

	pH	Total alkalinity ($CaCO_3$)	Total hardness ($CaCO_3$)	Temperature (F)	Flow volume (cfs)
East Canal	7.5	120	100	54	60
No. 4 Canal	7.3	84	65	48	70

Table 2. Glyphosate concentrations (ppb) in water from two canals treated with glyphosate at 150 ppb.

Sampling site (miles)	Sampling interval (min.)		Concentration (ppb)	
	East Canal	No. 4 Canal	East Canal	No. 4 Canal
0.2	1	1	28	16
	9	10	153	149
	17	19	116	150
	25	28	123	161
	33	37	125	154
	41	46	118	145
	49	55	114	--[a]
	57	64	5	24
1.0	1	1	ND[b]	ND
	10	13	63	78
	19	25	127	109
	28	37	118	109
	37	49	100	106
	46	61	122	96
	55	73	124	21
	64	85	37	ND
3.0	1	1	4	ND
	10	15	64	21
	19	29	129	--
	28	43	124	--
	37	57	127	--
	46	71	116	65
	55	85	64	18
	64	99	12	ND
5.0	1	1	4	ND
	11	16	49	34
	21	31	66	74
	31	46	92	91
	41	61	119	108
	51	76	93	74
	61	91	23	16
	71	106	6	4
7.0	--	1	--	5
	--	16	--	31
	--	31	--	55
	--	46	--	103
	--	61	--	99
	--	76	--	61
	--	91	--	20
	--	106	--	4
9.0	--	1	--	ND
	--	17	--	19
	--	33	--	64
	--	49	--	90
	--	65	--	76
	--	81	--	48
	--	97	--	20
	--	113	--	5

[a] Not reported.

[b] Not detected; detection limit was 2.5 ppb.

CASE GS0178 GLYPHOSATE STUDY 23 PM 25 06/16/83

CHEM 103601 Isopropylamine Glyphosate

BRANCH EFB DISC 30 TOPIC

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00039381-E CONTENT CAT 0
Blackburn, R.D. 1975. Dissipation of glyphosate from pond water. In Determination of residues of glyphosate and its metabolite in aquatic use of Roundup herbicide.

SUBST. CLASS = S.

DIRECT RVW TIME = 8 1/2 (MH) START-DATE END DATE

REVIEWED BY: W. Frantz
TITLE: Staff Scientist
ORG: Dynamac Corp., Enviro Control Division, Rockville, MD
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SIGNATURE: W. Frantz DATE: Apr. 22, 1985

APPROVED BY:
TITLE:
ORG:
TEL:

SIGNATURE: DATE:

CONCLUSIONS:

Field Dissipation - Aquatic and Aquatic Impact Uses

1. This study is scientifically valid.

2. Glyphosate (4 lb/gal, formulation unspecified) dissipated from a pond in Florida, treated at 460 ppb, with a half-life of between 14 and 21 days. Less than 1% of the applied was detected in the pond water 127 days posttreatment. Glyphosate was detected at a maximum concentration of 0.46 ppb in bottom sediments sampled 63 days posttreatment. The glyphosate degradate aminomethyhlphosphonic acid was not detected (<2.5 ppb) in bottom sediments.

3. This study does not fulfill EPA Data Requirements for Registering Pesticides because pond water and sediment were not characterized, the pattern of formation and decline of the degradate aminomethylphosphonic acid could not be determined because the data were illegible, more than one pesticide was applied to the test site and may have affected the dissipation of glyphosate from water, and the pattern of formation and decline of degradates other than aminomethylphosphonic acid was not addressed.

MATERIALS AND METHODS:

A pond (0.843 A in surface area x 6.3 ft average depth), located in Ft. Lauderdale, was treated with a combination tank mix of glyphosate (MON 0139, 4 lb/gal, formulation and source unspecified), at 8 lb ai/A (460 ppb), and Sterox NJ (MON 0011, 4 lb/gal, formulation and source unspecified), at 8 lb ai/A. Water samples were taken pretreatment, and at 0, 1, 2, 5, 8, 24, 48, and 72 hours, and 7, 14, 21, 36, 63, and 127 days posttreatment from the surface, middle, and bottom of the pond at five locations. Bottom sediment samples, in triplicate, were taken pretreatment, and at 7, 14, 21, and 36 days after treatment.

Glyphosate and aminomethylphosphonic acid were determined in water and soil as reported in Monsanto Agriculture Report No. 325, described in Study 17 (00039381-C). Recovery values from water samples fortified with glyphosate and aminomethylphosphonic acid, at 2.5-500 ppb, were illegible. Detection limits were 2.5 ppb for both compounds.

REPORTED RESULTS:

Glyphosate dissipated from a pond in Florida with a half-life of between 14 and 21 days (Table 1). Weighted average glyphosate concentrations decreased from 85.6% of the applied at 1 hour posttreatment to <1% of the applied 127 days after a pond in Florida was treated with glyphosate at 460 ppb. The distribution of glyphosate in the surface, middle, and bottom waters of the pond is presented in Table 1. Aminomethylphosphonic acid concentrations in water were illegible. The concentration of glyphosate in bottom sediment samples ranged from 0.15 to 0.46 ppb. Aminomethyphosphonic acid was not detected in any bottom sediment samples. Neither glyphosate nor aminomethylphosphonic acid were detected in water or sediment control samples.

DISCUSSION:

1. The pattern of formation and decline of the degradate aminomethylphosphonic acid could not be determined because the reported concentrations were illegible.

2. Sediment characteristics, such as textural analysis, pH, organic matter content, and CEC, were not submitted. Additionally, water characteristics such as oxygen content and suspended solids, were not presented.

3. Recovery values for glyphosate and aminomethylphosphonic acid could not be determined because the values were illegible.

4. More than one pesticide was applied to the test pond and may have affected the dissipation of glyphosate from water.

5. The formulation of both pesticides was described only as 4 lb/gal.

Table 1. Glyphosate concentrations in pond water treated with glyphosate at 460 ppb.

Sampling interval	Surface	Middle	Bottom	Weighted average	Percent of applied
	ppb				
1 hour	732	357	70	394	85.6
2	725	287	60	364	79.2
5	828	375	135	453	98.5
8	728	351	110	403	87.6
24	412	472	245	379	82.5
48	362	393	330	362	78.2
72	343	351	315	337	73.2
7 days	264	199	268	243	52.9
14	197	275	297	255	55.5
21	145	135	119	133	29.0
36	73	69	80	74	16.1
63	23	22	21	22	4.8
127	<5	<5	<5	<5	<1.0

[a] Average of duplicate samples; samples corrected for recovery values.

[b] Weighted average determined by:

(34.1% x ppb surface) + (34.1% x ppb middle) + (31.8% x ppb bottom)

Table 2. Glyphosate concentrations (ppb) in bottom sediments of a pond treated with glyphosate at 460 ppb.

Sampling interval (days)	Glyphosate	Aminomethylphosphonic acid
0 (control)	ND[a]	ND[a]
7	0.22	ND
14	0.27	ND
21	0.27	ND
36	0.15	ND
63	0.46	ND
127	0.24	ND

[a] Not detected; detection limit was 2.5 ppb.